SUPPORTING INFORMATION

Palladium(II)-Catalysed Electrophilic Cyclisation of Electron-Deficient Aromatic Enynes

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1. General information

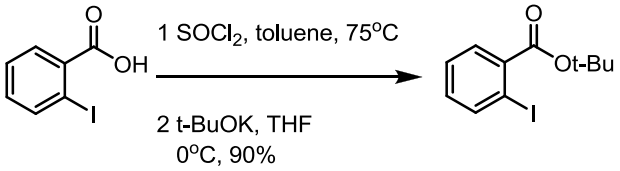
Reactions were performed under nitrogen unless otherwise stated. All reagents were purchased from Aldrich and used as received. Solvents (AR grade) were used as received. ^{1}H NMR and ^{13}C {^{1}H} spectra were recorded using Bruker Avance 400, Bruker DRX 500, Avance 600 or Varian VNMRS 700 spectrometers in $CDCl_3$ with residual solvent protons (7.26 ppm) or the carbon resonance (77.16 ppm) used to reference the spectra. Chromatography was carried out using silica gel (Silicagel LC60A 40-63 μm) obtained from Fluorochem. The removal of solvent was performed on a rotary evaporator under vacuum. IR spectra were recorded on a Perkin-Elmer 1615 FTRIR spectrophotometer. Melting points were determined using an Electrothermal melting point apparatus. Low resolution mass spectrometry was carried out on a Waters TQD equipped with Acquity UPLC and an electrospray ion source and high resolution mass spectrometry was performed on a Waters LCT Premier XE equipped with Acquity UPLC and a lock-mass electrospray ion source.

2. Experimental procedures and characterisation data

2.1 Synthesis of substituted styrene alkynone precursors and characterisation data

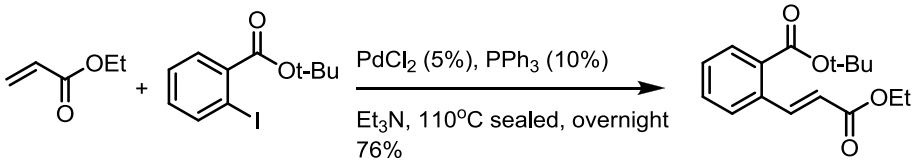
2-Vinylbenzoic acid, (*E*, *Z*)-2-styrylbenzoic acid and (*E*, *Z*)-2-(4-methylstyryl)benzoic acid were prepared according to literature methods.[1,2]

***tert*-Butyl 2-iodobenzoate**



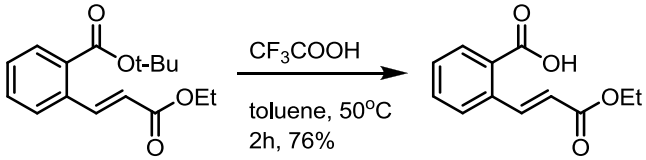
To a solution of 2-iodobenzoic acid (4.96 g, 20 mmol) in toluene (100 mL) was added 2 drops of *N*,*N*-dimethylformamide and thionyl chloride (1.69 mL, 24 mmol) and the reaction was stirred at 75 ºC overnight. After concentration *in vacuo*, the 2-iodobenzoyl chloride was added dropwise to a solution of potassium *t*-butoxide in THF (100 mL) at 0 ºC under nitrogen protection for 0.5 h. Filtration through a Celite pad and concentration *in vacuo* gave the product as a colorless oil (5.46 g, 90%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.62 (s, 9H), 7.08-7.13 (m, 1H), 7.35-7.39 (m, 1H), 7.67-7.70 (m, 1H), 7.93-7.95 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 28.1, 82.6, 93.4, 127.8, 130.4, 131.9, 137.4, 140.9, 166.1; FT-IR (neat) ν 2079, 1713, 1296, 1128 cm^{-1}; HRMS (ESI^{+}) m/z Calcd for $C_{11}H_{14}IO_2$ [M+H^{+}] 305.0033 found 305.0035.

(*E*)-*tert*-Butyl 2-(3-ethoxy-3-oxoprop-1-enyl)benzoate



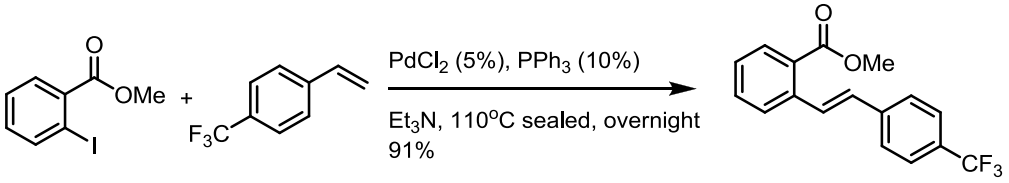
To a solution of $PdCl_2$ (0.159 g, 0.9 mmol) and PPh_3 (0.472 g, 1.8 mmol) in dry Et_3N (40 mL) under N_2 protection was added *tert*-butyl 2-iodobenzoate (5.46 g, 18 mmol) and ethyl acrylate (2.1 mL, 19.8 mmol). The reaction mixture was stirred at 110 ºC in a sealed tube overnight. After cooling and concentrating *in vacuo*, the residue was purified by flash chromatography on silica gel (2.5 cm × 20 cm, eluting with ethyl acetate/n-hexane = 1:7, R_f (EtOAc/hexane (1:5)) = 0.53) to give the corresponding Heck coupling product as a yellow oil(3.78 g, 76%): ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.33 (t, J = 7 Hz, 3H), 1.61 (s, 9H), 4.27 (q, J = 7 Hz, 2H), 6.27 (d, J = 16 Hz, 1H), 7.39-7.42 (m, 1H), 7.47-7.50 (m, 1H), 7.54-7.55 (m, 1H), 7.88-7.89 (m, 1H), 8.38 (d, J = 16 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 14.4, 28.3, 60.6, 82.3, 120.5, 127.8, 129.4, 130.7, 131.8, 132.3, 135.8, 144.4, 166.4, 166.7; FT-IR (neat) ν 1706, 1636, 1367, 1298, 1268, 1162, 765 cm^{-1}; HRMS (ESI$^+$) m/z Calcd for $C_{16}H_{20}O_4Na$ [M+Na$^+$] 299.1259 found 299.1266.

(*E*)-2-(3-Ethoxy-3-oxoprop-1-enyl)benzoic acid



Trifluoroacetic acid (8 mL) was injected into *tert*-butyl 2-(3-ethoxy-3-oxoprop-1-enyl)benzoate in toluene (50 mL) and the reaction was stirred at 50 ºC for 2 h. After concentration *in vacuo* and purification by flash chromatography on silica gel (2.5 cm × 20 cm, eluting with ethyl acetate/n-hexane = 1:3, R_f (EtOAc/hexane (1:5)) = 0.19), the product was isolated as a colorless oil (3.78 g, 76%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.35 (t, J = 7 Hz, 3H), 4.29 (q, J = 7 Hz, 2H), 6.33 (d, J = 16 Hz, 1H), 7.45-7.49 (m, 1H), 7.56-7.63 (m, 2H), 8.10-8.12 (m, 1H), 8.56 (d, J = 16 Hz, 1H), 10.8 (br.s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 14.4, 60.8, 121.5, 128.3, 128.7, 129.5, 131.8, 133.3, 137.3, 143.9, 166.8, 172.0; FT-IR (neat) ν 2982, 2656, 2360, 1706, 1636, 1304, 1170, 761 cm^{-1}; HRMS (ESI$^+$) m/z Calcd for $C_{12}H_{13}O_4$ [M+H$^+$] 221.0814 found 221.0803.

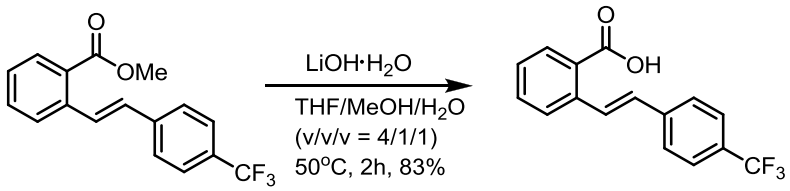
(*E*)-Methyl 2-(4-(trifluoromethyl)styryl)benzoate



To a solution of $PdCl_2$ (0.035 g, 0.2 mmol) and PPh_3 (0.1048 g, 0.4 mmol) in dry

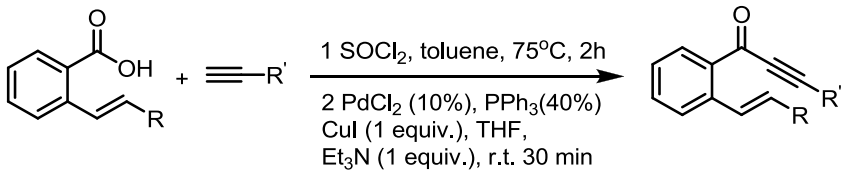
Et_3N (4 mL) under N_2 protection was added methyl 2-iodobenzoate (0.61 mL, 4 mmol) and 1-(trifluoromethyl)-4-vinyl benzene (0.71 mL, 4.8 mmol). The reaction mixture was stirred at 110 ºC in a sealed tube overnight. The reaction was cooled, concentrated *in vacuo* and the residue purified by flash chromatography on silica gel (2.5 cm × 20 cm, eluting with ethyl acetate/n-hexane = 1:20, R_f (EtOAc/hexane (1:15)) = 0.50) to give the corresponding Heck coupling product as a white solid (1.12 g, 91%): m.p. 73-74 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.94 (s, 3H), 7.00 (d, J = 16 Hz, 1H), 7.37 (t, J = 8 Hz, 1H), 7.53 (d, J = 8 Hz, 1H), 7.62 (dd, J_1 = 4 Hz, J_2 = 9 Hz, 4H), 7.71 (d, J = 8 Hz, 1H), 7.98 (d, J = 8 Hz, 1H), 8.12 (d, J = 16 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 52.2, 124.4 (q, J_{CF} = 270 Hz, CF_3), 125.6 (q, J_{CF} = 4 Hz, arene C), 127.0, 127.2, 127.8, 128.8, 129.5 (q, J_{CF} = 32 Hz, arene C), 129.8, 130.3, 130.9, 132.4, 138.8, 141.0, 167.7; FT-IR (neat) ν 2956, 1713, 1614, 1323, 1105, 951, 821 cm^{-1}; HRMS (ESI$^+$) m/z Calcd for $C_{17}H_{14}O_2F_3$ [M+H$^+$] 307.0940 found 307.0941.

(*E*)-2-(4-(Trifluoromethyl)styryl)benzoic acid



(*E*)-Methyl 2-(4-(trifluoromethyl)styryl)benzoate (0.98 g, 3.2 mmol) was dissolved in 6 mL of THF:MeOH:H_2O (4:1:l, v:v:v) and LiOH (405 mg, 9.6 mmol) was added at room temperature. The reaction mixture was then heated to 50 ºC for 2 h. After the reaction mixture was cooled to room temperature, it was acidified to pH 6 using 1M HCl. The product was extracted with ethyl acetate (2 x 20 mL) and then washed with water and brine. The extract was dried over anhydrous $MgSO_4$ and the solvent was evaporated *in vacuo* to give the stilbene carboxylic acid as a white solid (0.78 g, 83%): m.p. 132-134 ºC; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.04 (d, J = 16 Hz, 1H), 7.43 (t, J = 8 Hz, 1H), 7.60-7.66 (m, 5H), 7.76 (d, J = 8 Hz, 1H), 8.14 (d, J = 8 Hz, 1H), 8.16 (d, J = 16 Hz, 1H), 11.72 (br s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 124.3 (q, J_{CF} = 270 Hz, CF_3), 125.8 (q, J_{CF} = 4 Hz, arene C), 126.7, 127.2, 127.7, 128.0, 129.8 (q, J_{CF} = 32 Hz, arene C), 130.3, 130.4, 131.9, 133.5, 139.8, 140.9, 172.2; FT-IR (neat) ν 1682, 1415, 1327, 1108, 1069, 821, 746, 649 cm^{-1}; HRMS (ASAP$^+$) m/z Calcd for $C_{16}H_{12}O_2F_3$ [M+H$^+$] 293.0789 found 293.0788.

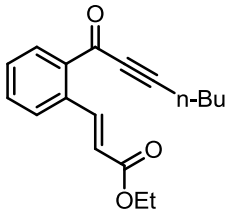
2.2 General procedure for synthesis of substituted styrene alkynone substrates and product characterisation data



To a solution of substituted 2-vinylbenzoic acid (1 mmol) in dry toluene (10 mL) was added 2 drops of *N*,*N*-dimethylformamide and thionyl chloride (0.09 mL, 1.2 mmol)

and the reaction mixture was stirred at 75 ºC for 2 h. Evaporation *in vacuo* gave the acid chloride. To a solution of the acid chloride in THF (10 mL), $PdCl_2$ (17.6 mg, 0.1 mmol), PPh_3 (104.8 mg, 0.4 mmol) and CuI (190 mg, 1 mmol) under N_2 protection was added stoichiometric amounts of the different alkynes. Finally, Et_3N (0.14 mL, 1 mmol) was added dropwise under N_2 protection. The reaction was stirred at room temperature for 0.5 h, concentrated *in vacuo* and the residue was purified by flash chromatography on silica gel to give the corresponding substituted styrene alkynones.

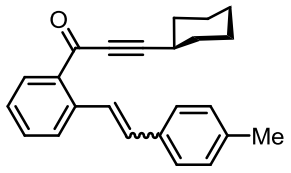
(*E*)-Ethyl 3-(2-hept-2-ynoylphenyl)acrylate



1a

Silica gel purification (2.5 cm × 20 cm, eluted with ethyl acetate/n-hexane = 1:8, R_f (EtOAc/hexane (1:5)) = 0.40) gave a brown yellow oil (45%): ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.96 (t, J = 7 Hz, 3H), 1.34 (t, J = 7 Hz, 3H), 1.47-1.51 (m, 2H), 1.63-1.66 (m, 2H), 2.49 (t, J = 7 Hz, 2H), 4.27 (q, J = 7 Hz, 2H), 6.29 (d, J = 16 Hz, 1H), 7.49-7.51 (m, 1H), 7.55-7.57 (m, 2H), 8.19 (d, J = 8 Hz, 1H), 8.41 (d, J = 16 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 13.6, 14.5, 19.1, 22.2, 29.9, 60.7, 81.1, 97.5, 121.6, 128.4, 129.4, 132.6, 133.1, 136.3, 136.4, 143.9, 166.6, 179.2; FT-IR (neat) ν 2203, 1711, 1636, 1242, 1176, 912, 762, 714 cm^{-1}; HRMS (ESI$^+$) m/z Calcd for $C_{18}H_{21}O_3$ [M+H$^+$] 285.1485 found 285.1489.

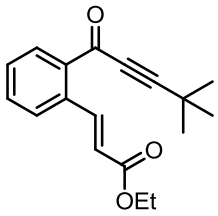
(*E*,*Z*)-3-Cyclohexyl-1-(2-(4-methylstyryl)phenyl)prop-2-yn-1-one



1b

Silica gel purification (2.5 cm × 25 cm, eluted with ethyl acetate/n-hexane = 1:50, R_f (EtOAc/hexane (1:10)) = 0.63) gave a brown oil (21%): ^{1}H NMR ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.35-1.37 (m, 3H), 1.55-1.62 (m, 3H), 1.72-1.78 (m, 2H), 1.87-1.92 (m, 2H), 2.27 (s, 1H), 2.37 (s, 2H), 2.64-2.69 (m, 1H), 6.63 (d, J = 12 Hz, 0.3H), 6.94-6.97 (m, 1.3H), 7.00-7.03 (m, 1H), 7.17 (d, J = 8 Hz, 1.3H), 7.24 (d, J = 7 Hz, 0.3H), 7.32 (dt, J_1 = 2 Hz, J_2 = 7 Hz, 0.3H), 7.34-7.38 (m, 1H), 7.45-7.46 (m, 1.3H), 7.52-7.54 (m, 0.7H), 7.72 (d, J = 8 Hz, 0.7H), 7.96 (dd, J = 16 Hz, 0.7H), 8.15-8.17 (m, 0.7H), 8.21-8.22 (m, 0.3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 21.3, 21.4, 24.9, 24.9, 25.8, 25.8, 29.5, 29.6, 31.8, 31.8, 81.1, 81.6, 99.9, 100.1, 126.6, 127.0, 127.1, 127.2, 128.9, 129.3, 129.5, 129.8, 130.3, 131.5, 131.9, 132.6, 132.6, 132.7, 132.8, 134.0, 134.8, 135.4, 136.0, 136.8, 138.0, 139.3, 139.6, 179.4, 180.3; FT-IR (neat) ν 2924, 2854, 2200, 1630, 1446, 1239, 918, 806 cm^{-1}; HRMS (ESI$^+$) m/z Calcd for $C_{24}H_{25}O_1$ [M+H$^+$] 329.1905 found 329.1900.

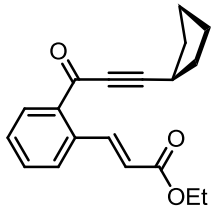
(*E*)-Ethyl 3-(2-(4,4-dimethylpent-2-ynoyl)phenyl)acrylate



1c

Silica gel purification (2.5 cm × 20 cm, eluted with ethyl acetate/n-hexane = 1:5, R_f (EtOAc/hexane (1:5)) = 0.50) gave a yellow oil (37%): ^{1}H NMR (700 MHz, $CDCl_3$) δ 1.34 (t, J = 7 Hz, 3H), 1.36 (s, 9H), 4.28 (q, J = 7 Hz, 2H), 6.30 (d, J = 16 Hz, 1H), 7.49-7.51 (m, 1H), 7.55-7.58 (m, 2H), 8.13-8.14 (m, 1H), 8.39 (d, J = 16 Hz, 1H); ^{13}C NMR (176 MHz, $CDCl_3$) δ 14.5, 28.2, 30.2, 60.7, 79.7, 104.6, 121.6, 128.4, 129.4, 132.4, 133.0, 136.2, 136.7, 143.8, 166.6, 179.4; FT-IR (neat) ν 2972, 2208, 1713, 1640, 1263, 1176, 759 cm^{-1}; HRMS (ESI$^+$) m/z Calcd for $C_{18}H_{21}O_3$ 285.1485 [M+H$^+$] found 285.1489.

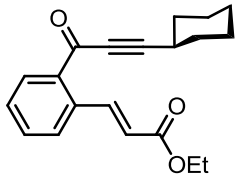
(*E*)-Ethyl 3-(2-(3-cyclopentylpropioloyl)phenyl)acrylate



1d

Silica gel purification (2.5 cm × 20 cm, eluted with ethyl acetate/n-hexane = 1:5, R_f (EtOAc/hexane (1:5)) = 0.38) gave a brown oil (39%): ^{1}H NMR (600 MHz, CD_2Cl_2) δ 1.32 (t, J = 7 Hz, 3H), 1.64 (m, 2H), 1.79 (m, 4H), 2.0-2.1 (m, 2H), 2.92 (t, J = 7 Hz, 1H), 4.25 (q, J = 7 Hz, 2H), 6.30 (d, J = 16 Hz, 1H), 7.51-7.53 (m, 1H), 7.57-7.60 (m, 2H), 8.19 (d, J = 8 Hz, 1H), 8.32 (d, J = 16 Hz, 1H); ^{13}C NMR (150 MHz, CD_2Cl_2) δ 14.5, 25.6, 30.7, 33.7, 60.9, 80.7, 101.7, 121.6, 128.6, 129.7, 132.9, 133.3, 136.3, 136.8, 144.0, 166.7, 179.5; FT-IR (neat) ν 2956, 2203, 1711, 1635, 1243, 1176, 946, 764 cm^{-1}; HRMS (ESI$^+$) m/z Calcd for $C_{19}H_{21}O_3$ [M+H$^+$] 297.1491 found 297.1483.

(*E*)-Ethyl 3-(2-(3-cyclohexylpropioloyl)phenyl)acrylate

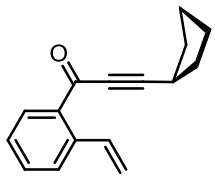


1e

Silica gel purification (2.5 cm × 20 cm, eluted with ethyl acetate/n-hexane = 1:5, R_f (EtOAc/hexane (1:5)) = 0.50) gave a brown oil (54%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.32-1.38 (m, 6H), 1.56-1.65 (m, 3H), 1.74-1.77 (m, 2H), 1.90-1.92 (m, 2H), 2.67-2.71 (m, 1H), 4.27 (q, J = 7 Hz, 2H), 6.29 (d, J = 16 Hz, 1H), 7.48-7.54 (m, 1H), 7.56-7.57 (m, 2H), 8.17-8.19 (m, 1H), 8.40 (d, J = 16 Hz, 1H); ^{13}C NMR (125 MHz,

$CDCl_3$) δ 14.4, 24.8, 25.8, 29.5, 31.7, 60.7, 81.0, 101.0, 121.5, 128.4, 129.4, 132.6, 133.0, 136.2, 136.6, 143.9, 166.6, 179.3; FT-IR (neat) ν 2930, 2855, 2198, 1710, 1635, 1240, 1175, 915, 763 cm^{-1}; HRMS (ESI^+) m/z Calcd for $C_{20}H_{23}O_3$ $[M+H^+]$ 311.1647 found 311.1642.

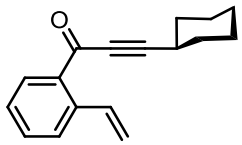
3-Cyclopentyl-1-(2-vinylphenyl)prop-2-yn-1-one



1f

Silica gel purification (2.5 cm × 25 cm, eluted with ethyl acetate/n-hexane = 1:50, R_f (EtOAc/hexane (1:20)) = 0.33) gave a brown oil (41%): ^1H NMR (400 MHz, $CDCl_3$) δ 1.59-1.67 (m, 2H), 1.75-1.82 (m, 4H), 2.00-2.07 (m, 2H), 2.86-2.93 (m, 1H), 5.37 (dd, J_1 = 1 Hz, J_2 = 11 Hz, 1H), 5.66 (dd, J_1 = 1 Hz, J_2 = 17 Hz, 1H), 7.37-7.41 (m, 1H), 7.46-7.53 (m, 2H), 7.56-7.59 (m, 1H), 8.13 (dd, J_1 = 1 Hz, J_2 = 8 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 25.4, 30.5, 33.4, 81.0, 100.6, 116.9, 127.5, 127.7, 132.5, 132.9, 135.3, 136.1, 139.5, 180.1; FT-IR (neat) ν 2958, 2869, 2204, 1640, 1242, 768 cm^{-1}; HRMS (ESI^+) m/z Calcd for $C_{16}H_{17}O_1$ $[M+H^+]$ 225.1274 found 225.1274.

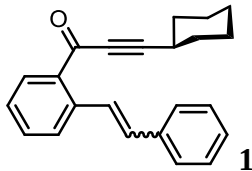
3-Cyclohexyl-1-(2-vinylphenyl)prop-2-yn-1-one



1g

Silica gel purification (2.5 cm × 25 cm, eluted with ethyl acetate/n-hexane = 1:40, R_f (EtOAc/hexane (1:20)) = 0.50) gave a colorless oil (17%) (decomposed partly in $CDCl_3$ overnight): ^1H NMR (700 MHz, $CDCl_3$) δ 1.34-1.43 (m, 3H), 1.59-1.61 (m, 3H), 1.75-1.78 (m, 2H), 1.91-1.92 (m, 2H), 2.67 (m, 1H), 5.37 (dd, J_1 = 1 Hz, J_2 = 11 Hz, 1H), 5.67 (dd, J_1 = 1 Hz, J_2 = 17 Hz, 1H), 7.38-7.40 (m, 1H), 7.49-7.53 (m, 2H), 7.57-7.58 (m, 1H), 8.15 (dd, J_1 = 1 Hz, J_2 = 8 Hz, 1H); ^{13}C NMR (176 MHz, $CDCl_3$) δ 24.9, 25.8, 29.6, 31.8, 81.3, 100.0, 116.9, 127.5, 127.7, 132.6, 132.9, 135.3, 136.1, 139.6, 180.1; FT-IR (neat) ν 2926, 2853, 2200, 1640, 1563, 1240, 915, 768 cm^{-1}; HRMS (ESI^+) m/z Calcd for $C_{17}H_{19}O_1$ $[M+H^+]$ 239.1430 found 239.1431.

(*E*,*Z*)-3-Cyclohexyl-1-(2-styrylphenyl)prop-2-yn-1-one

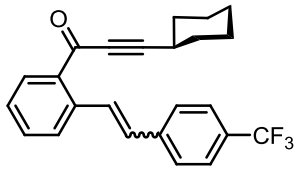


1h

Silica gel purification (2.5 cm × 25 cm, eluted with ethyl acetate/n-hexane = 1:20, R_f (EtOAc/hexane (1:10)) = 0.50) gave a yellow oil (48%): ^1H NMR (400 MHz, $CDCl_3$) δ 1.24-1.29 (m, 3H), 1.43-1.53 (m, 3H), 1.63-1.69 (m, 2H), 1.77-1.81 (m, 2H),

2.53-2.61 (m, 1H), 6.29 (d, *J* = 12 Hz, 0.3H), 6.92-7.00 (m, 1.7H), 7.05-7.06 (m, 1H), 7.17-7.23 (m, 1H), 7.28-7.32 (m, 2H), 7.43-7.49 (m, 2H), 7.62-7.64 (m, 1H), 7.92 (d, *J* = 16 Hz, 1H), 8.07-8.10 (m, 0.7H), 8.13-8.16(m, 0.3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 24.8, 24.9, 25.8, 25.8, 29.5, 29.6, 31.7, 31.8, 81.5, 84.2, 100.0, 100.2, 127.0, 127.1, 127.2, 127.3, 127.7, 128.0, 128.1, 128.8, 129.4, 130.3, 130.7, 131.5, 131.9, 132.6, 132.7, 132.7, 132.9, 135.5, 136.0, 136.9, 137.5, 139.1, 139.3, 179.3, 180.2; FT-IR (neat) *v* 2928, 2853, 2360, 2200, 1737, 1640, 1447, 1240, 916, 759, 692 cm^{-1}; HRMS (ESI$^+$) m/z Calcd for $C_{23}H_{23}O_1$ [M+H$^+$] 315.1749 found 315.1739.

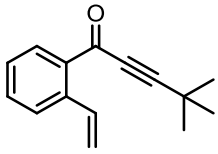
3-Cyclohexyl-1-(2-(4-(trifluoromethyl)styryl)phenyl)prop-2-yn-1-one



1i

After the reaction, the mixture was filtered through a Celite pad which was washed with diethyl ether and concentrated *in vacuo* to give the crude product as a colorless oil (6%). This material was used in the next step without further purification. R_f (EtOAc/hexane (1:15)) = 0.50.

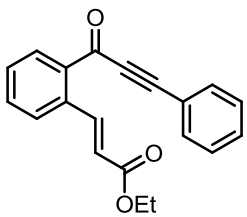
4, 4-Dimethyl-1-(2-vinylphenyl)pent-2-yn-1-one



1j

Silica gel purification (2.5 cm × 25 cm, eluted with ethyl acetate/n-hexane = 1:15, R_f (EtOAc/hexane (1:15)) = 0.41) gave a colorless oil (92%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.36 (s, 9H), 5.37 (d, J_1 = 1 Hz, J_2 = 11 Hz, 1H), 5.66 (dd, J_1 = 1 Hz, J_2 = 17 Hz, 1H), 7.37-7.41 (m, 1H), 7.46-7.53 (m, 2H), 7.56-7.59 (m, 1H), 8.10-8.12 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 28.2, 30.3, 80.0, 103.5, 116.9, 127.5, 127.7, 132.4, 132.8, 135.4, 136.1, 139.5, 180.0; FT-IR (neat) *v* 2970, 2209, 1644, 1263, 1225, 1045, 884, 768, 668 cm^{-1}; HRMS (ESI$^+$) m/z Calcd for $C_{15}H_{17}O_1$ [M+H$^+$] 213.1274 found 213.1275.

(*E*)-Ethyl 3-(2-(3-phenylpropioloyl)phenyl)acrylate

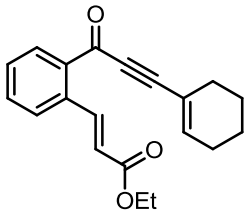


1k

Silica gel (2.5 cm × 25 cm, eluted with ethyl acetate/n-hexane = 1:5, R_f (EtOAc/hexane (1:3)) = 0.54) to give brown oil (15%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.32 (t, *J* = 7 Hz, 3H), 4.26 (q, *J* = 7 Hz, 2H), 6.34 (d, *J* = 16 Hz, 1H), 7.41-7.44 (m,

2H), 7.50 (tt, J_1 = 2 Hz, J_2 = 7 Hz, 1H), 7.54-7.57 (m, 1H), 7.59-7.62 (m, 2H), 7.66-7.68 (m, 2H), 8.30 (d, J = 8 Hz, 1H), 8.47 (d, J = 16 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.4, 60.8, 88.3, 93.7, 120.1, 121.8, 128.6, 128.8, 129.5, 131.1, 132.6, 133.2, 133.4, 136.3, 136.5, 143.7, 166.6, 178.9; FT-IR (neat) ν 2194, 1710, 1633, 1594, 1267, 1176, 994, 758 cm^{-1}; HRMS (ESI$^+$) m/z Calcd for $C_{20}H_{17}O_3$ [M+H$^+$] 305.1172 found 305.1175.

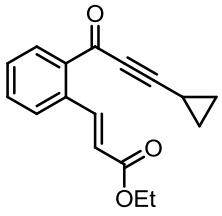
(*E*)-Ethyl 3-(2-(3-cyclohexenylpropioloyl)phenyl)acrylate



1l

Silica gel purification (2.5 cm × 25 cm, eluted with ethyl acetate/n-hexane = 1:5, R_f (EtOAc/hexane (1:5)) = 0.36) gave a yellow oil (39%) (decomposed in $CDCl_3$ overnight): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.34 (t, J = 7 Hz, 3H), 1.61-1.72 (m, 4H), 2.18-2.22 (m, 2H), 2.22-2.27 (m, 2H), 4.27 (q, J = 7 Hz, 2H), 6.30 (d, J = 16 Hz, 1H), 6.54-6.57 (m, 1H), 7.47-7.51 (m, 1H), 7.54-7.59 (m, 2H), 8.15-8.17 (m, 1H), 8.41 (d, J = 16 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.5, 21.2, 22.1, 26.4, 28.4, 60.7, 86.8, 96.3, 119.2, 121.5, 128.4, 129.4, 132.4, 133.0, 136.2, 136.7, 143.1, 143.9, 166.6, 179.2; HRMS (ESI$^+$) m/z Calcd for $C_{20}H_{20}O_3Na$ [M+Na$^+$] 331.1305 found 331.1307.

(*E*)-Ethyl 3-(2-(3-cyclopropylpropioloyl)phenyl)acrylate



1m

Silica gel purification (2.5 cm × 25 cm, eluted with ethyl acetate/n-hexane = 1:5, R_f (EtOAc/hexane (1:5)) = 0.25) gave a brown oil (44%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.00-1.06 (m, 4H), 1.35 (t, J = 7 Hz, 3H), 1.49-1.56 (m, 1H), 4.28 (q, J = 7 Hz, 2H), 6.29 (d, J = 16 Hz, 1H), 7.47-7.51 (m, 1H), 7.53-7.58 (m, 2H), 8.11-8.14 (m, 1H), 8.39 (d, J = 16 Hz, 1H); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 10.0, 14.3, 22.9, 31.8, 60.7, 76.9, 101.7, 121.4, 128.4, 129.5, 132.6, 133.1, 136.0, 143.8, 166.6, 178.8; FT-IR (neat): ν 2359, 2206, 1710, 1632, 1566, 1477, 1314, 1251, 1177, 914, 762 cm^{-1}; HRMS (ESI$^+$) m/z Calcd for $C_{17}H_{17}O_3$ [M+H$^+$] 269.1172 found 269.1174.

2.3 General procedure for substituted styrene alkynone cyclisation and product characterisation data

Procedure A

To AcOH (3 mL) containing $Pd(OAc)_2$ (10 mol %) and LiCl (4 equiv.), enyne (0.15 mmol) was added. The reaction was heated at 60 ºC in air until the substituted styrene alkynone disappeared, as monitored by GC-MS. On cooling, the solvent was removed *in vacuo* and the residue was purified by flash chromatography to give the product.

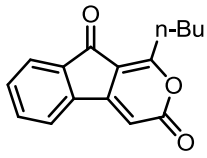
Procedure B

To AcOH (3 mL) containing $Pd(OAc)_2$ (10 mol %) and LiCl (4 equiv.), enyne (0.15 mmol) was added. The reaction was heated at 60 ºC under a nitrogen atmosphere. The mixture was stirred until the substituted styrene alkynone disappeared, as monitored by GC-MS. On cooling, the solvent was removed *in vacuo* and the residue was purified by flash chromatography to give the product.

Procedure C

To CH_3CN (3 mL) containing $PdCl_2$ (10 mol %), substrate (0.15 mmol) was added. The reaction was heated at 80 ºC under a nitrogen atmosphere. The mixture was stirred until the substituted styrene alkynone disappeared, as monitored by GC-MS. After cooling, the solvent was removed *in vacuo* and the residue was purified by flash chromatography to give the product.

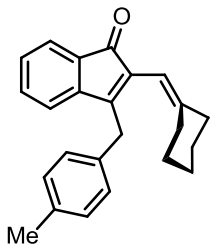
1-Butylindeno[2,1-c]pyran-3,9-dione



2a

Procedure A, silica gel purification (2.5 cm × 25 cm, eluted with ethyl acetate/n-hexane = 1:5, R_f (EtOAc/hexane (1:5)) = 0.20) gave a yellow, crystalline product (31%): m.p. 100-101 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.96 (t, J = 7 Hz, 3H), 1.41-1.50 (m, 2H), 1.73-1.81 (m, 2H), 3.09 (t, J = 8 Hz, 2H), 6.47 (s, 1H), 7.65 (dt, J_1 = 1 Hz, J_2 = 8 Hz, 1H), 7.72 (dt, J_1 = 1 Hz, J_2 = 7 Hz, 1H), 7.82 (dt, J_1 = 1 Hz, J_2 = 8 Hz, 1H), 7.89 (dt, J_1 = 1 Hz, J_2 = 8 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 13.8, 22.5, 29.2, 30.4, 102.6, 112.5, 123.5, 124.6, 133.1, 134.9, 139.0, 139.0, 153.5, 161.5, 170.5, 187.7; FT-IR (neat) ν 2971, 2928, 1732, 1699, 1633, 1578, 1462, 1363, 1140, 906, 874 cm^{-1}; HRMS (ESI$^+$) m/z Calcd for $C_{16}H_{15}O_3$ [M+H$^+$] 255.1021 found 255.1017.

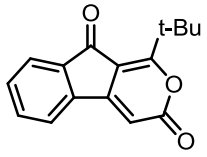
2-(Cyclohexylidenemethyl)-3-(4-methylbenzyl)-1H-inden-1-one



3b

Procedure C, silica gel purification (2.5 cm × 25 cm, eluted with ethyl acetate/n-hexane = 1:80, R_f (EtOAc/hexane (1:10)) = 0.53) gave a brown-red oil (53%): ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.56-1.58 (m, 4H), 1.63-1.64 (m, 2H), 2.15 (t, J = 5 Hz, 2H), 2.29 (dt, J_1 = 1 Hz, J_2 = 6 Hz, 2H), 2.31 (s, 3H), 3.85 (s, 2H), 5.74 (s, 1H), 6.84 (d, J = 7 Hz, 1H), 7.09-7.12 (m, 2H), 7.13-7.16 (m, 2H), 7.18-7.20 (m, 1H), 7.20 (dt, J_1 = 1 Hz, J_2 = 8 Hz, 1H), 7.38-7.39 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 21.2, 26.6, 28.0, 28.7, 31.9, 32.9, 37.4, 110.5, 120.4, 122.1, 128.2, 128.6, 129.5, 131.3, 133.4, 133.4, 134.0, 136.4, 145.6, 149.7, 156.0, 197.5; FT-IR (neat) v 2925, 2852, 1709, 1602, 1446, 1161, 810, 744 cm^{-1}; HRMS (ESI$^+$) m/z Calcd for $C_{24}H_{25}O_1$ [M+H$^+$] 329.1905 found 329.1886.

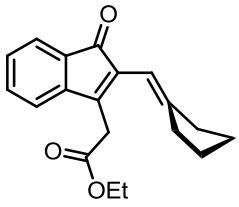
1-*tert*-Butylindeno[2,1-c]pyran-3,9-dione



2c

Procedure A, silica gel purification (2.5 cm × 25 cm, eluted with ethyl acetate/n-hexane = 1:10, R_f (EtOAc/hexane (1:5)) = 0.41) gave a white crystalline solid (24 h, 25%, 2 weeks, 67%): m.p. 224-225 ºC; ^{1}H NMR (700 MHz, $CDCl_3$) δ 1.52 (s, 9H), 6.50 (s, 1H), 7.64 (t, J = 8 Hz, 1H), 7.70 (t, J = 7 Hz, 1H), 7.79 (d, J = 8 Hz, 1H), 7.87 (d, J = 8 Hz, 1H); ^{13}C NMR (176 MHz, $CDCl_3$) δ 27.3, 38.8, 102.1, 111.9, 122.9, 124.6, 133.0, 134.8, 138.6, 139.0, 155.5, 161.0, 178.4, 186.9; FT-IR (neat) v 2971, 2928, 1732, 1699, 1633, 1578, 1462, 1276, 1254, 1182, 1049, 906, 874 cm^{-1}; HRMS (ESI$^+$) m/z Calcd for $C_{16}H_{15}O_3$ [M+H$^+$] 255.1021 found 255.1017.

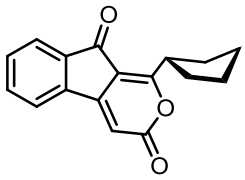
Ethyl 2-(2-(cyclopentylidenemethyl)-1-oxo-1H-inden-3-yl)acetate



3d

Procedure C, silica gel purification (2.5 cm × 25 cm, eluted with ethyl acetate/n-hexane = 1:15, R_f (EtOAc/hexane (1:5) = 0.41) gave a red oil (69%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.25 (t, J = 7 Hz, 3H), 1.64-1.71 (m, 4H), 2.30-2.31 (m, 2H), 2.46-2.47 (m, 2H), 3.55 (s, 2H), 4.18 (q, J = 7 Hz, 2H), 5.95 (t, J = 2 Hz, 1H), 7.06 (d, J = 7 Hz, 1H), 7.16-7.20 (m, 1H), 7.31-7.35 (m, 1H), 7.39-7.41 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.3, 25.8, 26.9, 32.1, 33.3, 35.0, 61.50, 109.3, 119.7, 122.4, 128.4, 130.7, 133.7, 135.0, 145.5, 148.1, 154.3, 169.3, 196.7; FT-IR (neat) v 2957, 1732, 1710, 1603, 1456, 1162, 1034, 754 cm^{-1}; HRMS (ESI$^+$) m/z Calcd for $C_{19}H_{21}O_3$ [M+H$^+$] 297.1485 found 297.1487.

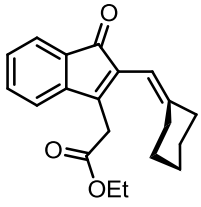
1-Cyclopentylindeno[2,1-c]pyran-3,9-dione



2d

Procedure A, silica gel purification (2.5 cm × 25 cm, eluted with ethyl acetate/n-hexane = 1:5, R_f (EtOAc/hexane (1:5)) = 0.25) gave a white, crystalline solid (34%): m.p. 186-187 ºC; ^{1}H NMR (700 MHz, $CDCl_3$) δ 1.74-1.75 (m, 2H), 1.88-1.95 (m, 4H), 2.03-2.05 (m, 2H), 4.14-4.19 (m, 1H), 6.44 (s, 1H), 7.64 (dt, J_1 = 1 Hz, J_2 = 7 Hz, 1H), 7.71 (dt, J_1 = 1 Hz, J_2 = 7 Hz, 1H), 7.81 (d, J = 8 Hz, 1H), 7.88 (d, J = 7 Hz, 1H); ^{13}C NMR (176 MHz, $CDCl_3$) δ 26.7, 31.4, 39.8, 102.5, 111.8, 123.5, 124.6, 133.1, 134.9, 139.0, 139.2, 153.7, 161.7, 173.5, 188.0; FT-IR (neat) ν 2954, 2866, 1730, 1700, 1650, 1616 cm^{-1}; HRMS (ASAP$^+$) m/z Calcd for $C_{17}H_{15}O_3$ [M+H$^+$] 267.1021 found 267.1011.

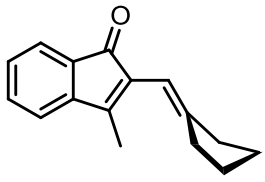
Ethyl 2-(2-(cyclohexylidenemethyl)-1-oxo-1H-inden-3-yl)acetate



3e

Procedure C, silica gel purification (2.5 cm × 25 cm, eluted with ethyl acetate/n-hexane = 1:15, R_f (EtOAc/hexane (1:5)) = 0.46) gave a red, crystalline solid (76%): m.p. 82-84 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.25 (t, J = 7 Hz, 3H), 1.54-1.56 (m, 4H), 1.60-1.64 (m, 2H), 2.08-2.11 (m, 2H), 2.27-2.30 (m, 2H), 3.53 (s, 2H), 4.19 (q, J = 7 Hz, 2H), 5.67 (s, 1H), 7.05-7.07 (m, 1H), 7.17-7.20 (m, 1H), 7.32-7.36 (m, 1H), 7.40-7.42 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 14.3, 26.5, 28.0, 28.6, 31.6, 33.4, 37.4, 61.5, 110.2, 119.8, 122.4, 128.5, 130.7, 133.7, 134.6, 145.4, 149.1, 150.3, 169.3, 197.2; FT-IR (neat): ν 2931, 2852, 1723, 1705, 1605, 1458, 1249, 1026, 774, 736 cm^{-1}; HRMS (ASAP) m/z Calcd for $C_{20}H_{22}O_3$ [M] 310.1569 found 310.1546.

2-(Cyclopentylidenemethyl)-3-methyl-1H-inden-1-one

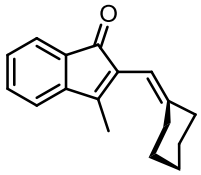


3f

Procedure C, silica gel purification (2.5 cm × 25 cm, eluted with ethyl acetate/n-hexane = 1:15, R_f (EtOAc/hexane (1:20)) = 0.34) gave a red oil (94%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.68-1.71 (m, 4H), 2.10 (s, 3H), 2.27-2.28 (m, 2H), 2.48-2.49 (m, 2H), 5.96 (s, 1H), 7.04 (d, J = 7 Hz, 1H), 7.17 (t, J = 7 Hz, 1H), 7.33 (dt, J_1 = 1 Hz, J_2 = 8 Hz, 1H), 7.37 (d, J = 7 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.0,

25.9, 26.9, 32.3, 34.8, 109.9, 118.9, 121.8, 128.4, 131.0, 133.1, 133.5, 146.7, 152.4, 153.1, 197.4; FT-IR (neat) *v* 2924, 1706, 1456, 1383, 962, 754 cm^{-1}; HRMS (ESI^+) m/z Calcd for $C_{16}H_{17}O_1$ [$M+H^+$] 225.1274 found 225.1274.

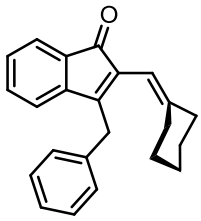
2-(Cyclohexylidenemethyl)-3-methyl-1H-inden-1-one



3g

Procedure C, silica gel purification (2.5 cm × 25 cm, eluted with ethyl acetate/n-hexane = 1:20, R_f (EtOAc/hexane (1:15)) = 0.53) gave a red oil (88%): ^1H NMR (400 MHz, $CDCl_3$) δ 1.56-1.64 (m, 6H), 2.09-2.10 (m, 5H), 2.29 (t, J = 6 Hz, 2H), 5.70 (s, 1H), 7.05 (d, J = 7 Hz, 1H), 7.18 (t, J = 8 Hz, 1H), 7.34 (dt, J_1 = 1 Hz, J_2 = 7 Hz, 1H), 7.39 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 13.0, 26.6, 27.8, 28.6, 31.7, 37.4, 110.9, 119.0, 121.9, 128.4, 131.0, 132.6, 133.5, 146.6, 148.6, 154.0, 197.8; FT-IR (neat) *v* 2926, 2852, 1706, 1610, 1456, 1382, 1082, 754 cm^{-1}; HRMS (ESI^+) m/z Calcd for $C_{17}H_{19}O_1$ [$M+H^+$] 239.1430 found 239.1431.

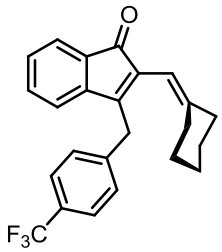
3-Benzyl-2-(cyclohexylidenemethyl)-1H-inden-1-one



3h

Procedure C, silica gel purification (2.5 cm × 25 cm, eluted with ethyl acetate/n-hexane = 1:80, R_f (EtOAc/hexane (1:10)) = 0.57) gave a red oil (78%): ^1H NMR (400 MHz, $CDCl_3$) δ 1.55-1.56 (m, 3H), 1.60-1.63 (m, 3H), 2.14 (t, J = 6 Hz, 2H), 2.28 (t, J = 6 Hz, 2H), 3.89 (s, 2H), 5.74 (s, 1H), 6.82 (d, J = 7 Hz, 1H), 7.12 (dt, J_1 = 1 Hz, J_2 = 8 Hz, 1H), 7.17-7.30 (m, 6H), 7.38-7.40 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 26.5, 28.0, 28.7, 31.9, 33.3, 37.4, 110.4, 120.4, 122.2, 126.8, 128.2, 128.7, 128.9, 131.3, 133.4, 133.5, 137.2, 145.5, 149.8, 155.7, 197.5; FT-IR (neat) *v* 2927, 2852, 1719, 1602, 1453, 760, 724, 697 cm^{-1}; HRMS (ESI^+) m/z Calcd for $C_{23}H_{23}O_1$ [$M+H^+$] 315.1749 found 315.1724.

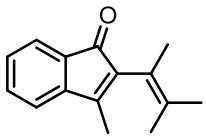
2-(Cyclohexylidenemethyl)-3-(4-(trifluoromethyl)benzyl)-1H-inden-1-one



3i

Procedure C, silica gel purification (2.5 cm × 25 cm, eluted with ethyl acetate/n-hexane = 1:30, R_f (EtOAc/hexane (1:15)) = 0.47) gave a red solid (98%): m.p. 123-125 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.53-1.57 (m, 4H), 1.60-1.64 (m, 2H), 2.13 (t, J = 6 Hz, 2H), 2.28 (t, J = 6 Hz, 2H), 3.9 (s, 2H), 5.7 (s, 1H), 6.79 (d, J = 7 Hz, 1H), 7.15 (dt, J_1 = 1 Hz, J_2 = 8 Hz, 1H), 7.21-7.25 (m, 1H), 7.38 (d, J = 8 Hz, 2H), 7.41-7.43 (m, 1H), 7.55 (d, J = 8 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 26.5, 28.0, 28.7, 32.0, 33.0, 37.4, 110.2, 120.1, 122.5, 124.3 (q, J_{CF} = 270 Hz, CF_3), 125.8 (q, J_{CF} = 4 Hz, arene C), 128.5, 129.0, 129.3 (q, J_{CF} = 32 Hz, arene C), 131.1, 133.6, 134.1, 141.4, 145.1, 150.4, 154.3, 197.1; FT-IR (neat) ν 2926, 2854, 1709, 1602, 1448, 1323, 1124, 1067, 1020, 848, 752 cm^{-1}; HRMS (ESI$^+$) m/z Calcd for $C_{24}H_{22}O_1F_3$ [M+H$^+$] 383.1617 found 383.1617.

3-Methyl-2-(3-methylbut-2-en-2-yl)-1H-inden-1-one

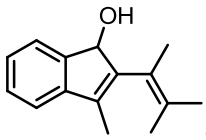


3j

Procedure C, silica gel purification (2.5 cm × 25 cm, eluted with ethyl acetate/n-hexane = 1:20, R_f (EtOAc/hexane (1:10)) = 0.50) gave a brown oil (98%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.58 (s, 3H), 1.82 (s, 6H), 2.03 (s, 3H), 7.06 (d, J = 7 Hz, 1H), 7.19 (t, J = 7 Hz, 1H), 7.35 (t, J = 8 Hz, 1H), 7.39 (d, J = 7 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 12.5, 18.6, 20.3, 22.6, 119.0, 120.1, 121.8, 128.4, 131.0, 132.3, 133.4, 138.3, 146.2, 154.1, 197.7; FT-IR (neat) ν 2914, 1702, 1608, 1455, 1380, 1324, 1081, 755, 719 cm^{-1}; HRMS (ESI$^+$) m/z Calcd for $C_{15}H_{17}O_1$ [M+H$^+$] 213.1279 found 213.1262.

2.4 Procedure for Luche reduction of cyclisation product and characterisation data

3-Methyl-2-(3-methylbut-2-en-2-yl)-1H-inden-1-ol



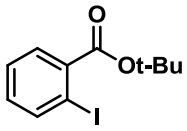
4j

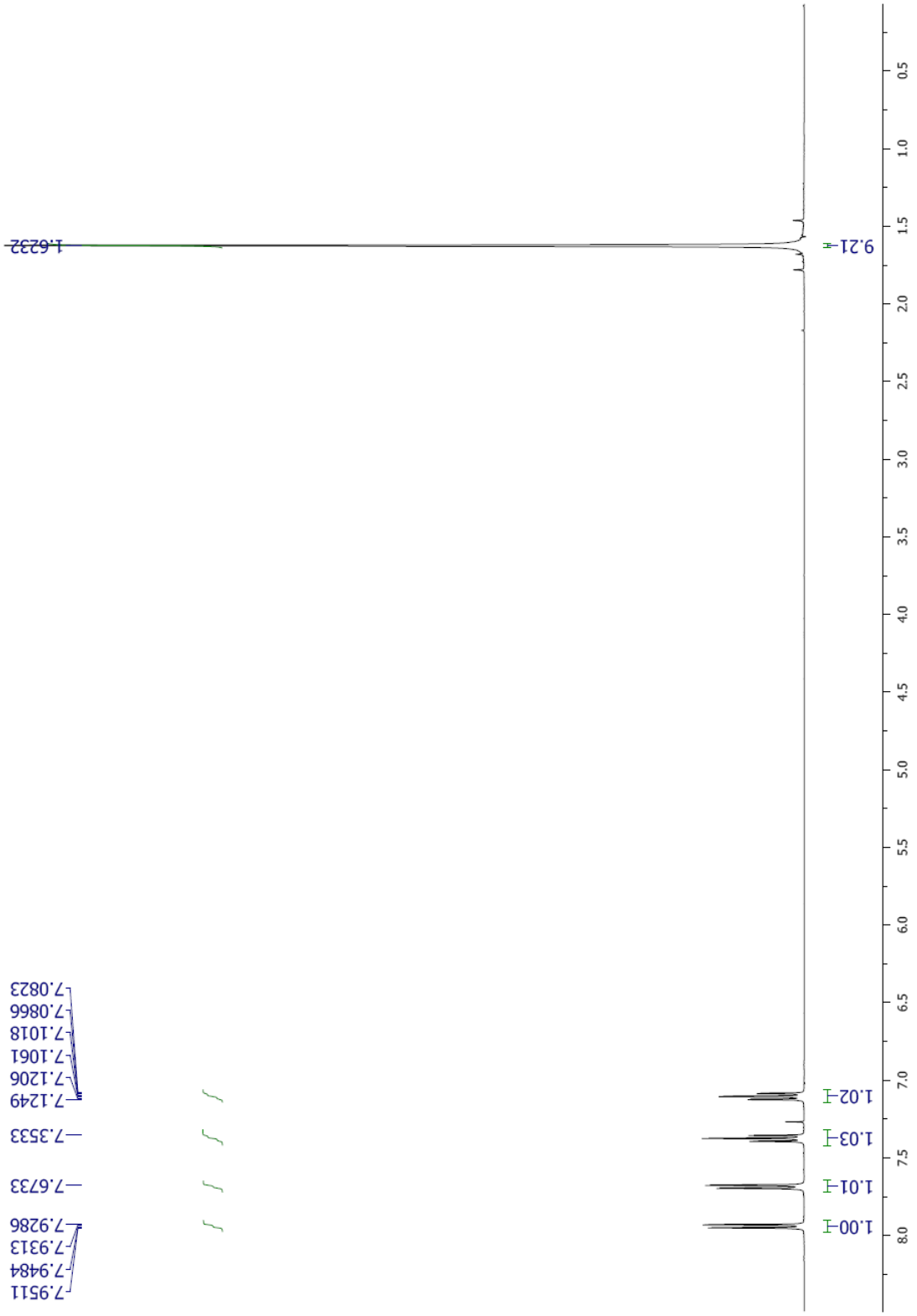
To MeOH (10 mL) containing cerium(III) chloride heptahydrate (1.1 equiv.) and substrate (0.45 mmol) was added sodium borohydride (1.1 equiv.) at 0 ºC. The reaction was stirred at room temperature under an N_2 atmosphere for 0.5 h. Then, the solvent was removed *in vacuo.* The residue was purified by flash chromatography (2.5 cm × 8 cm, eluted with ethyl acetate/n-hexane = 1:5, R_f (EtOAc/hexane (1:2)) = 0.62) to give a brown oil (90%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.65 (d, J = 1 Hz, 3H), 1.86 (s, 3H), 1.89 (s, 3H), 1.89 (s, 3H), 5.21 (s, 1H), 7.17-7.22 (m, 2H), 7.32 (dt, J_1 = 1 Hz, J_2 = 7 Hz, 1H), 7.50 (d, J = 8 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 11.5, 18.8, 20.5, 22.4, 77.2, 118.9, 123.1, 123.2, 125.6, 128.5, 131.1, 133.9, 144.7, 144.7, 147.5; FT-IR (neat) ν 1725, 1606, 1436, 1372, 1177, 1088, 1005, 752, 731, 688, 630 cm^{-1}.

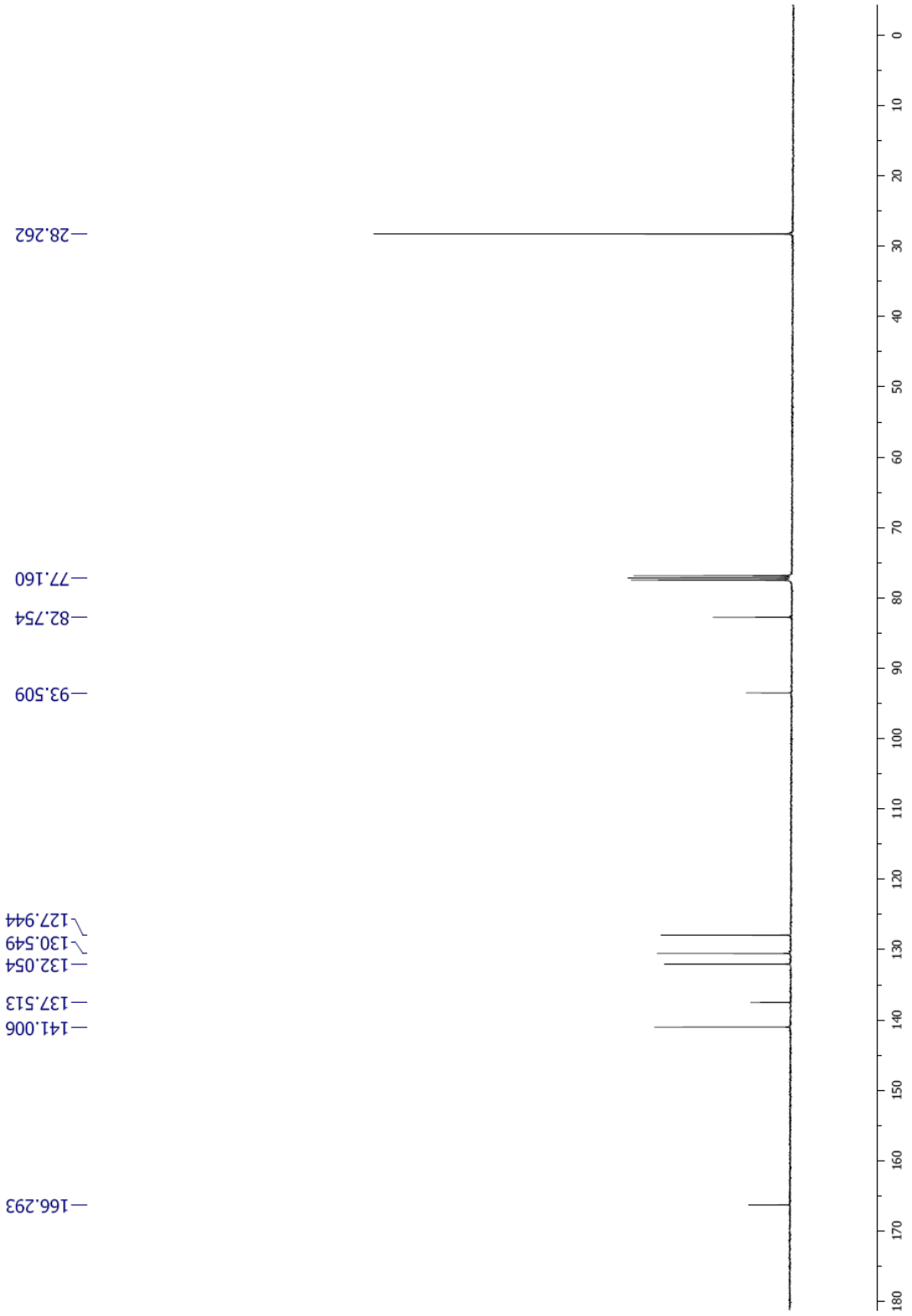
2.5 References

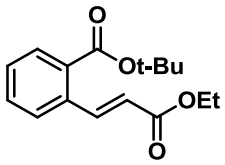
1. Shahzad, S. A.; Vivant, C.; Wirth, T. *Biochemistry*, **2009**, *48*, 6288.
2 Wang, M.; Zhou, H.; Wirz, M.; Tang, Y.; Boddy, C. N. *Org. Lett.*, **2010**, *12*, 1364.

3. ^{1}H and ^{13}C-NMR spectra for new compounds





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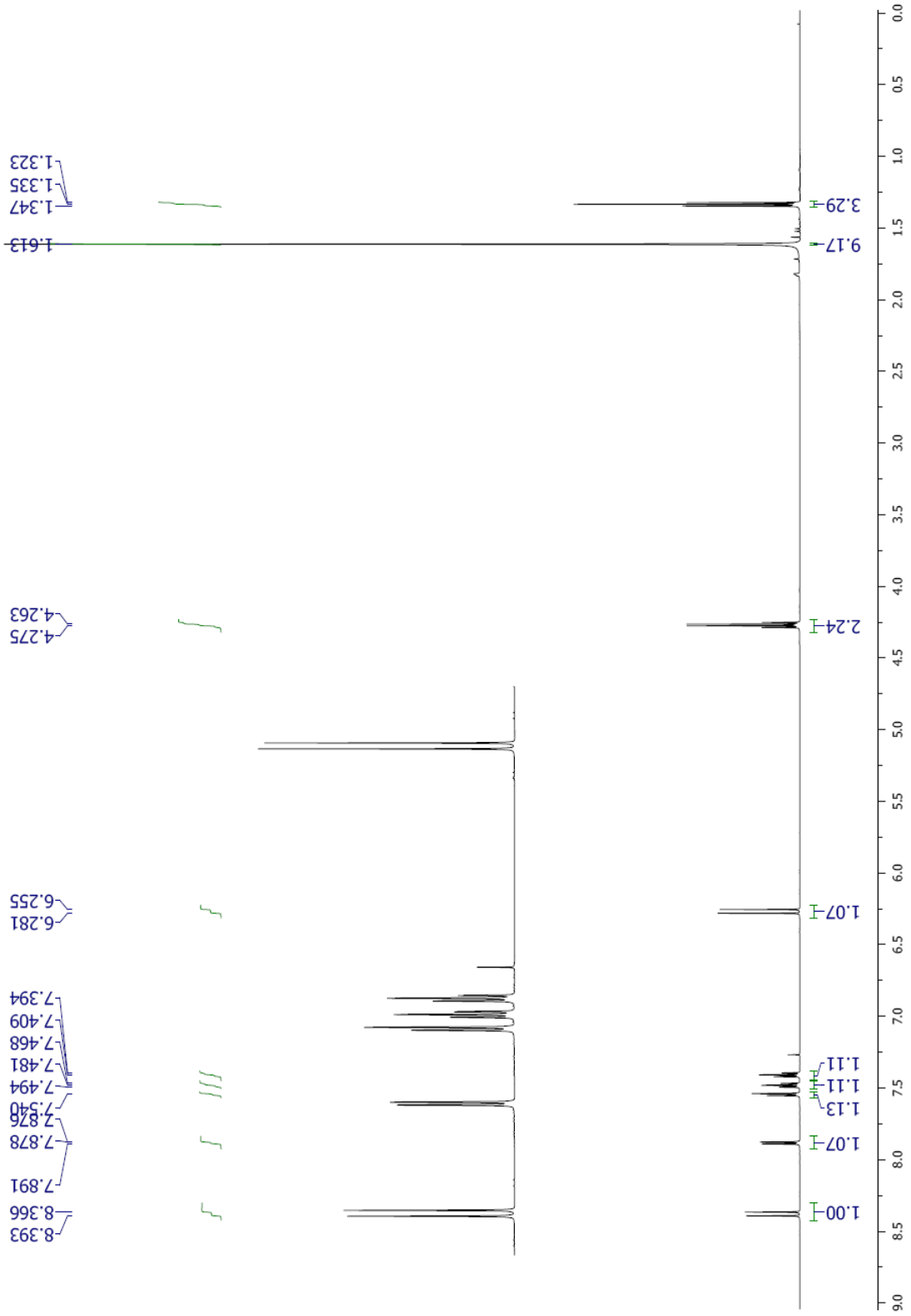
Ot-Bu
OEt
O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7.494
7.540
7.876
7.878
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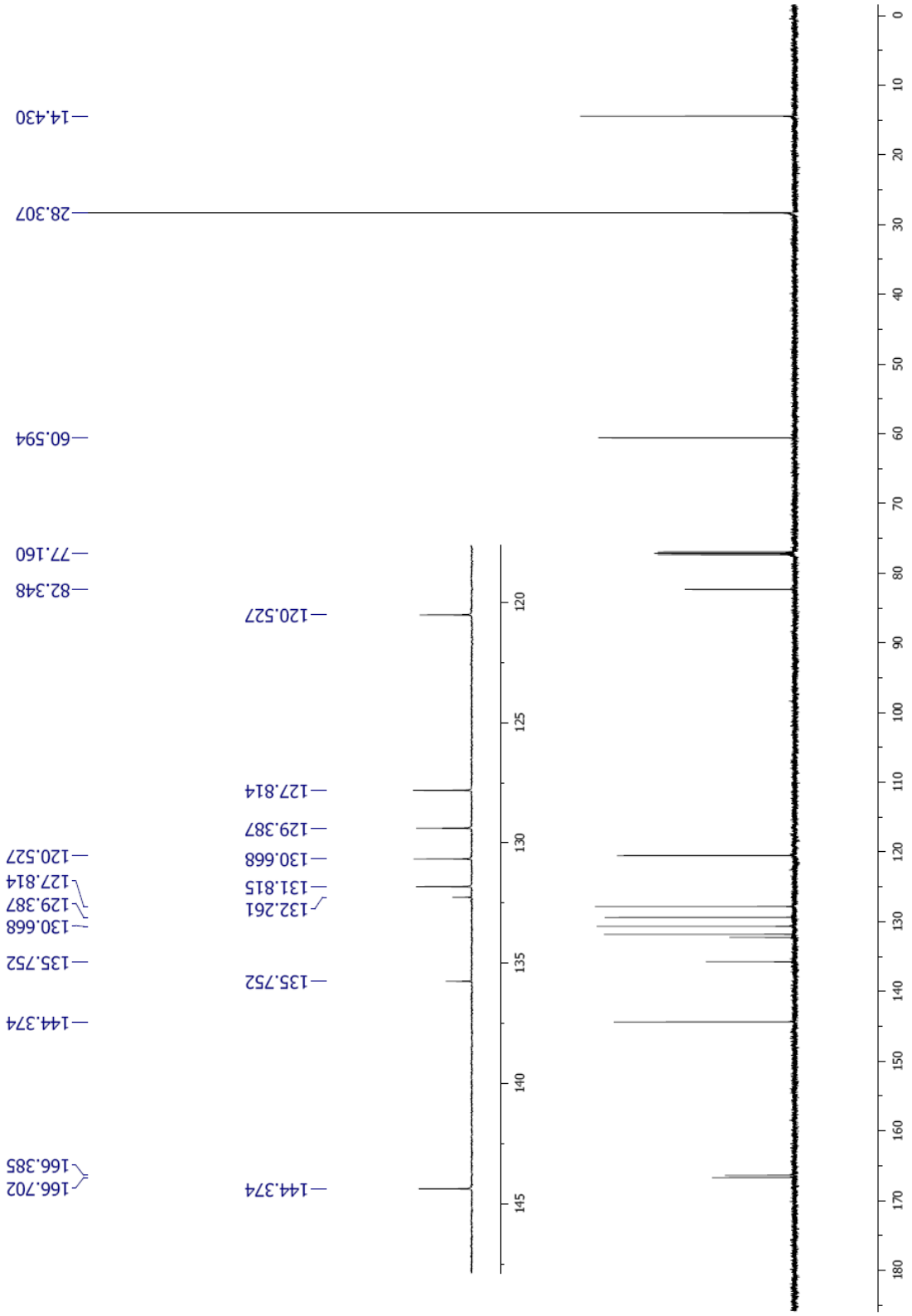
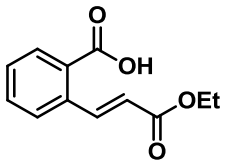
8.393
3.29
9.17
2.24
1.07
1.11
1.11
1.13
1.07
1.00

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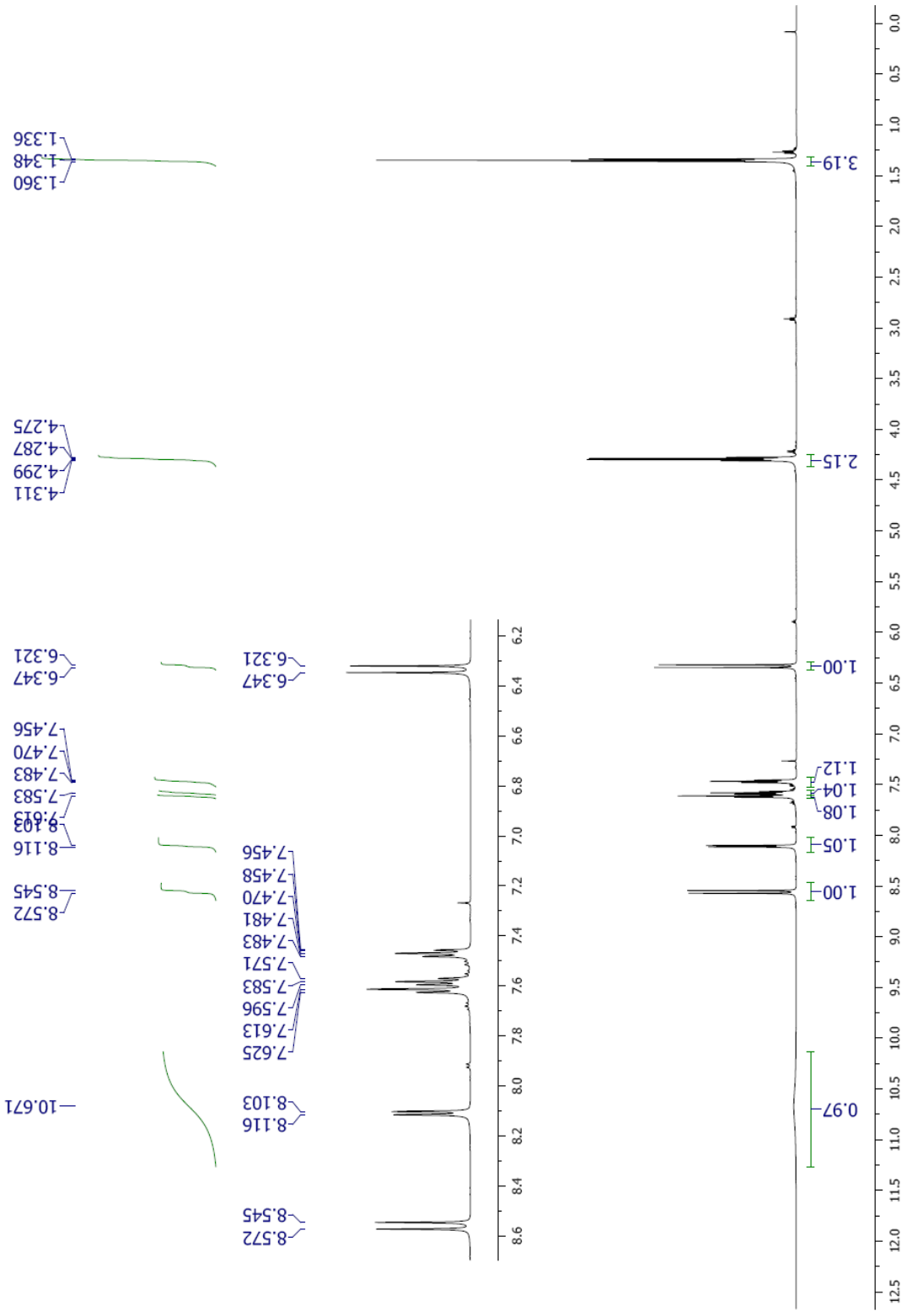
OH
OEt
O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6.321
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7.483
7.583
7.613
8.103
8.116
8.545
8.572
10.671
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1.12
1.04
1.08
1.05
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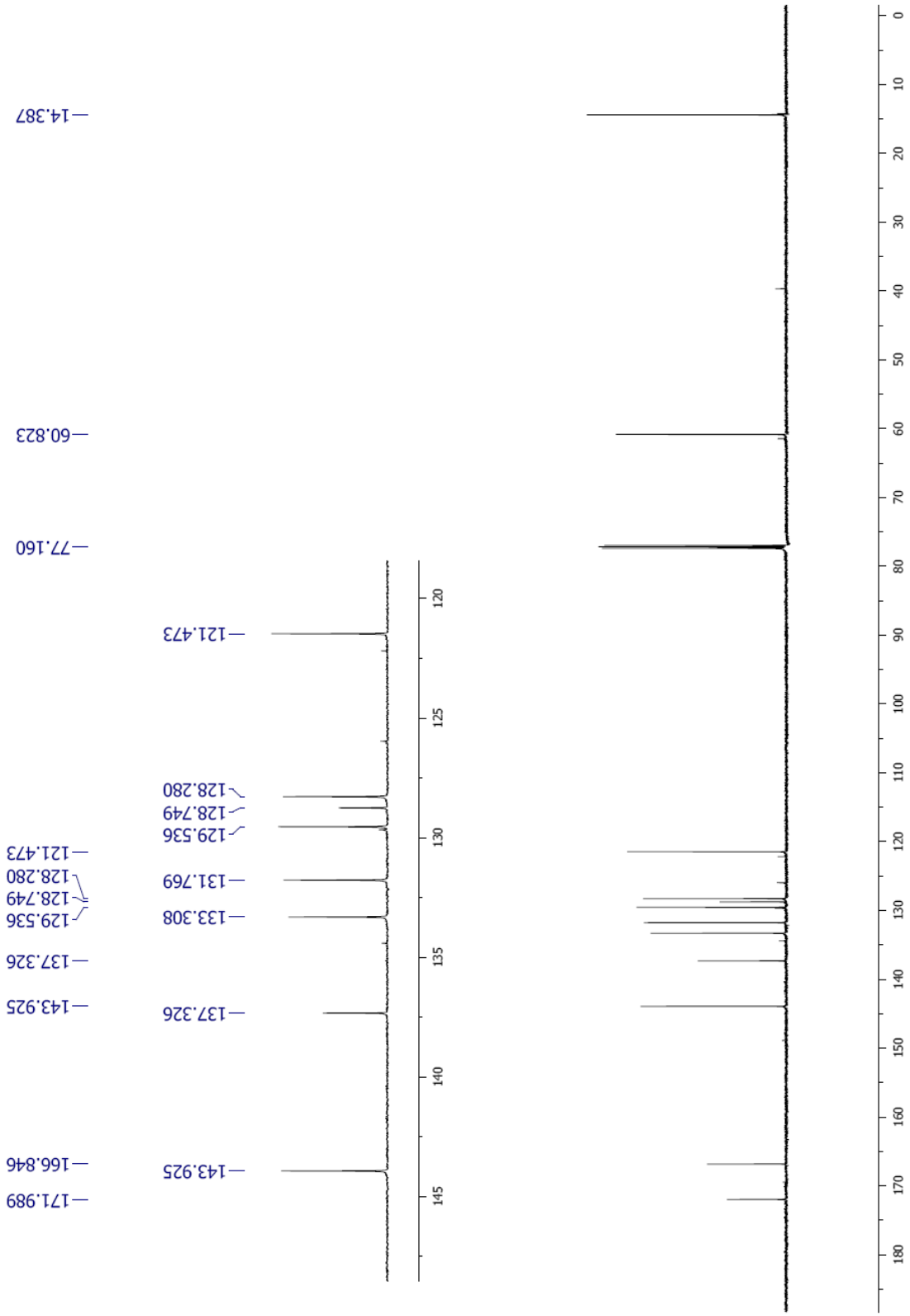

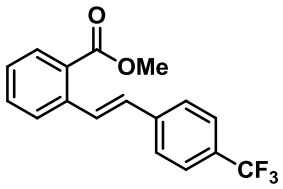
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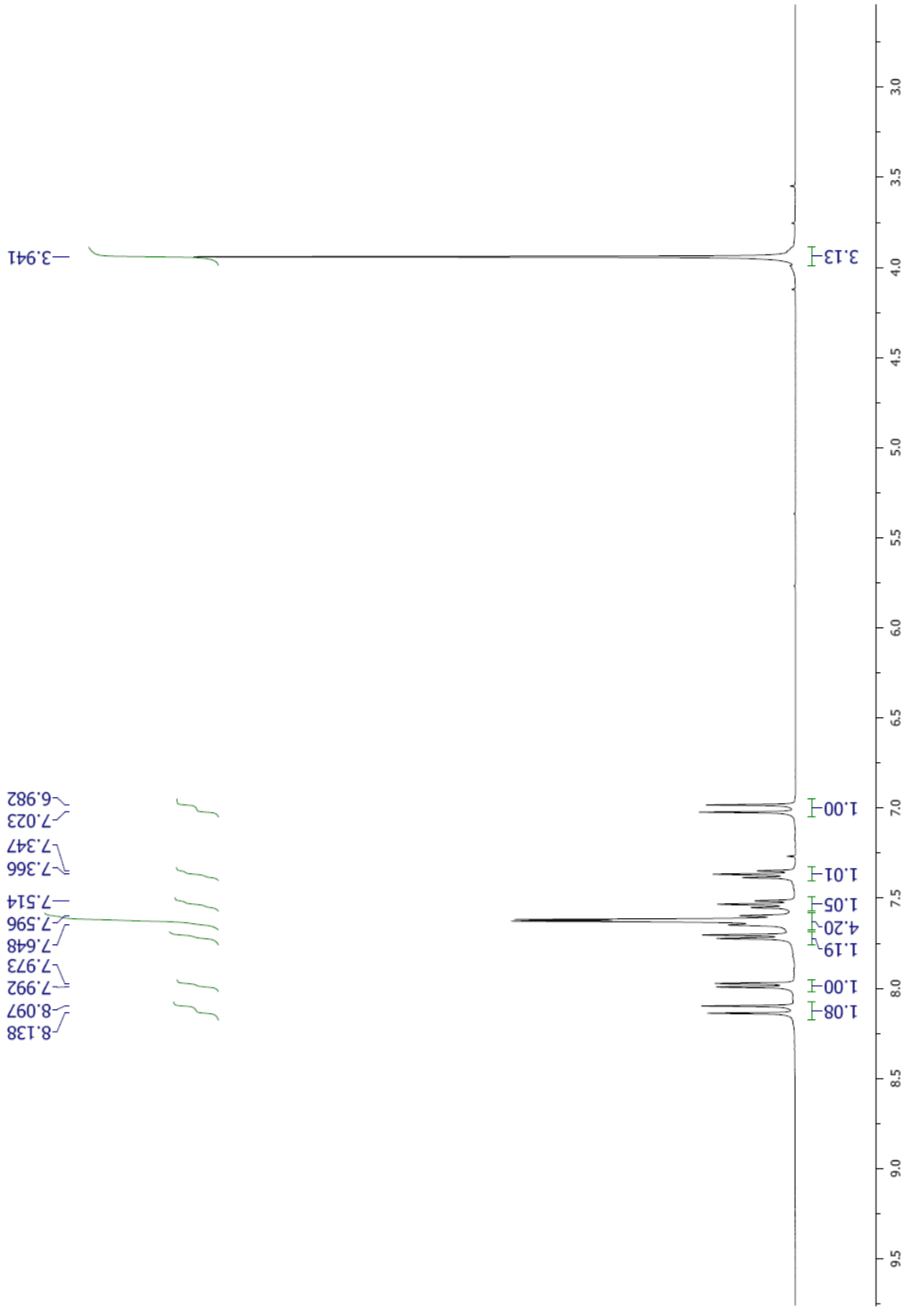
CF3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1.05
4.20
1.19
1.00
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3.5
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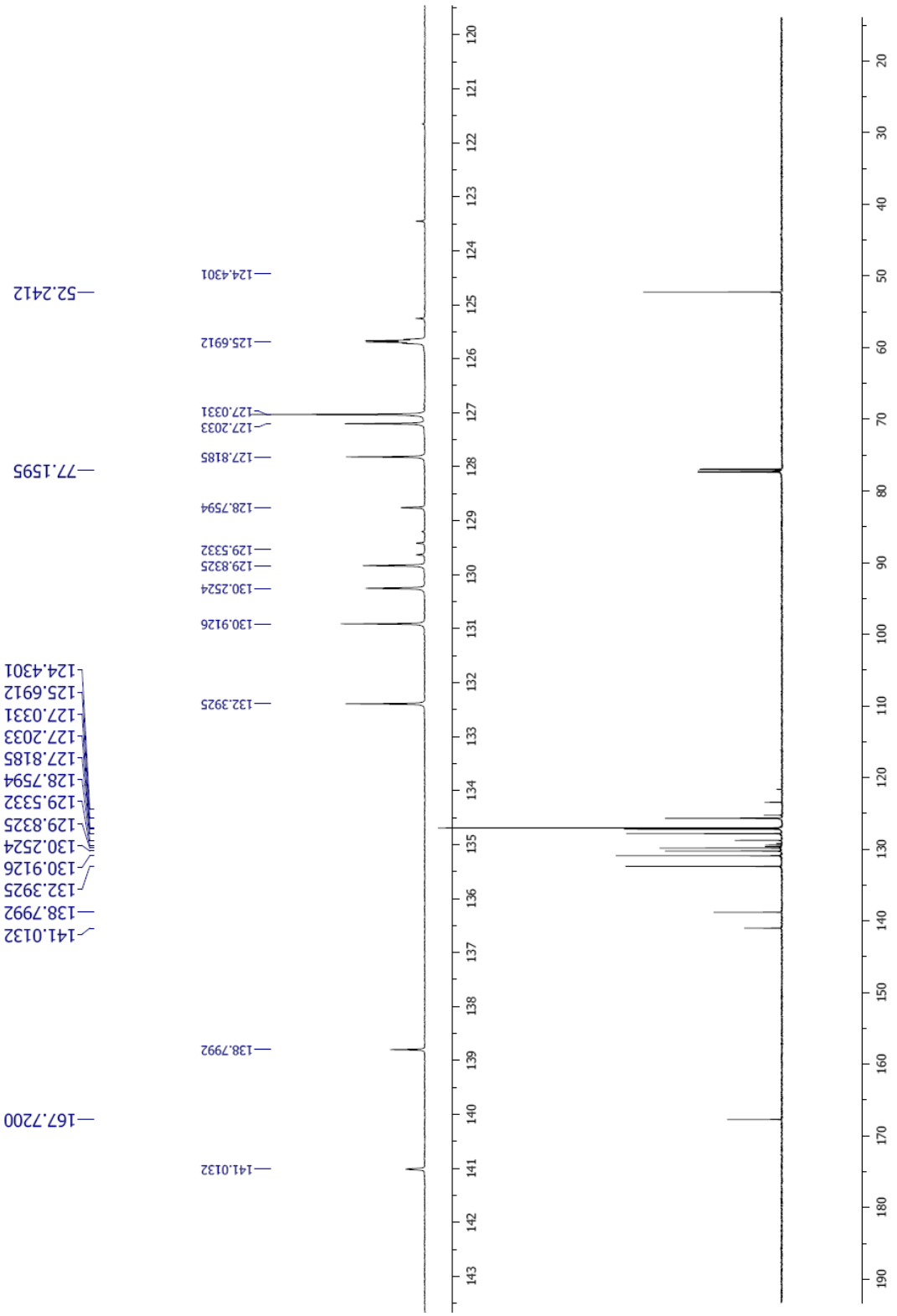
8.5
9.0
9.5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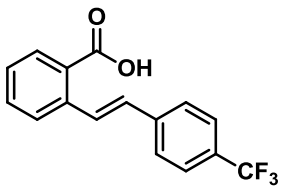

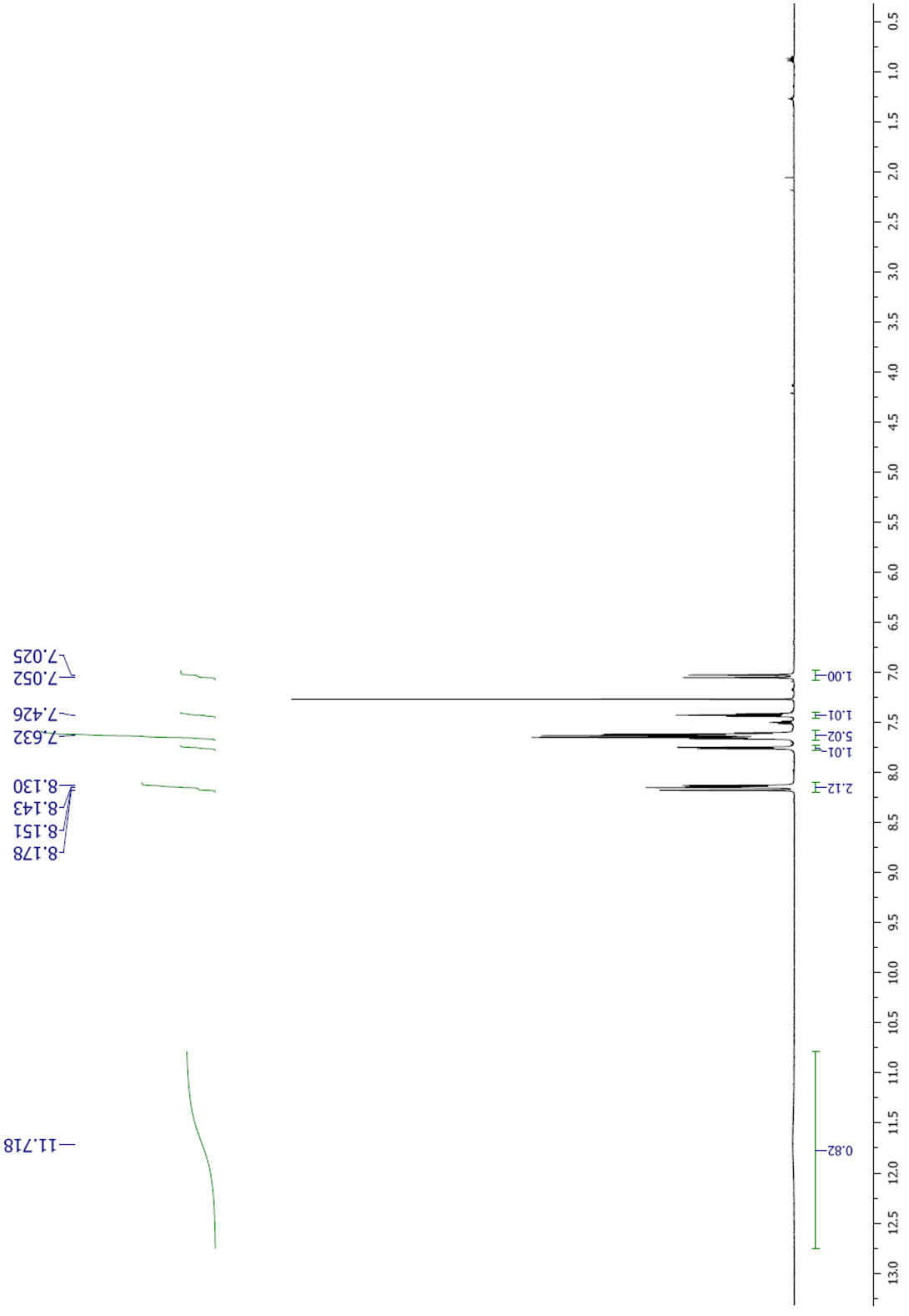

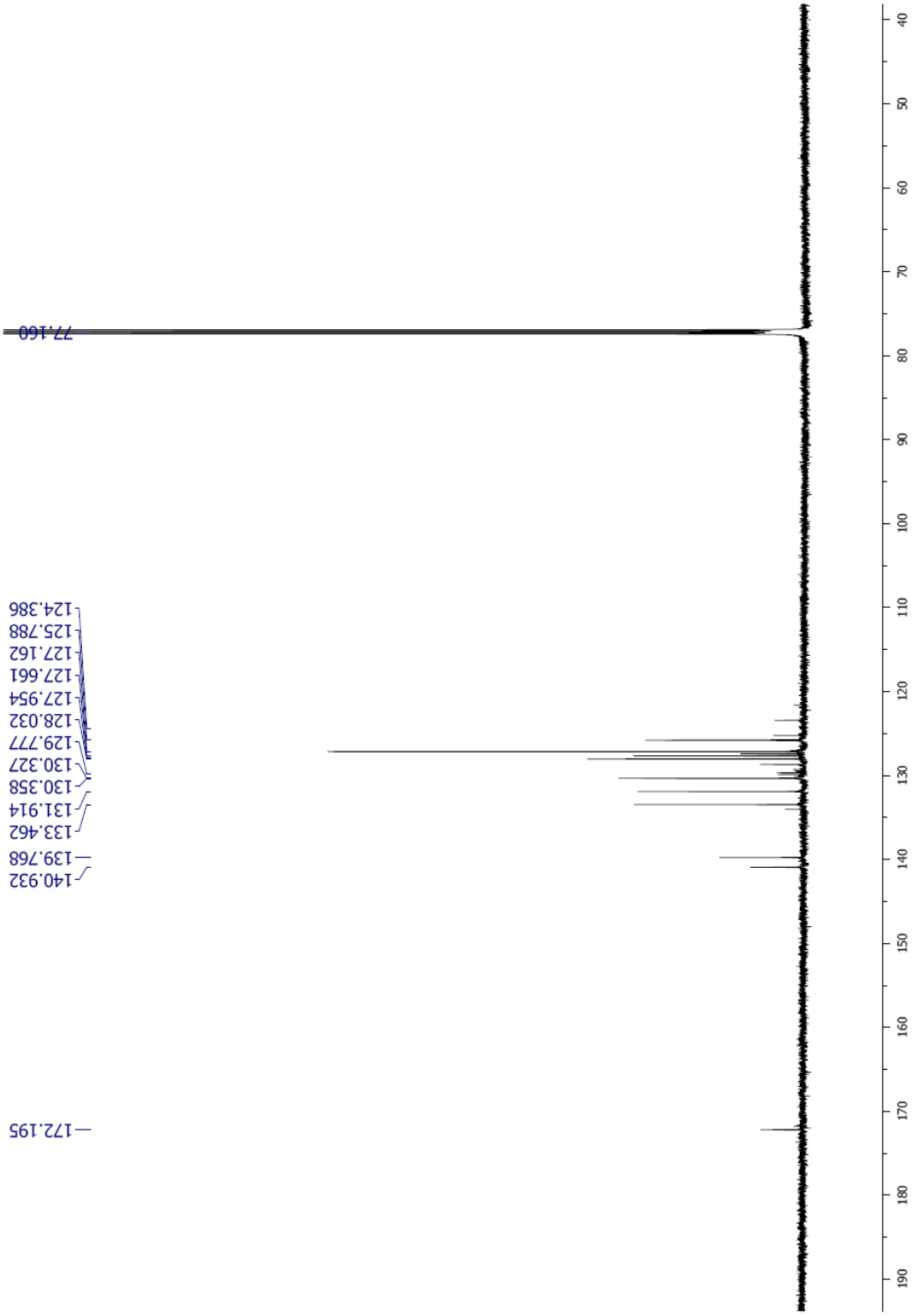
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139.768
140.932
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150
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180
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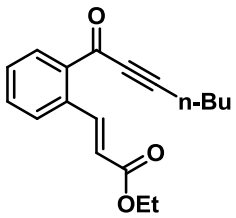
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n-Bu
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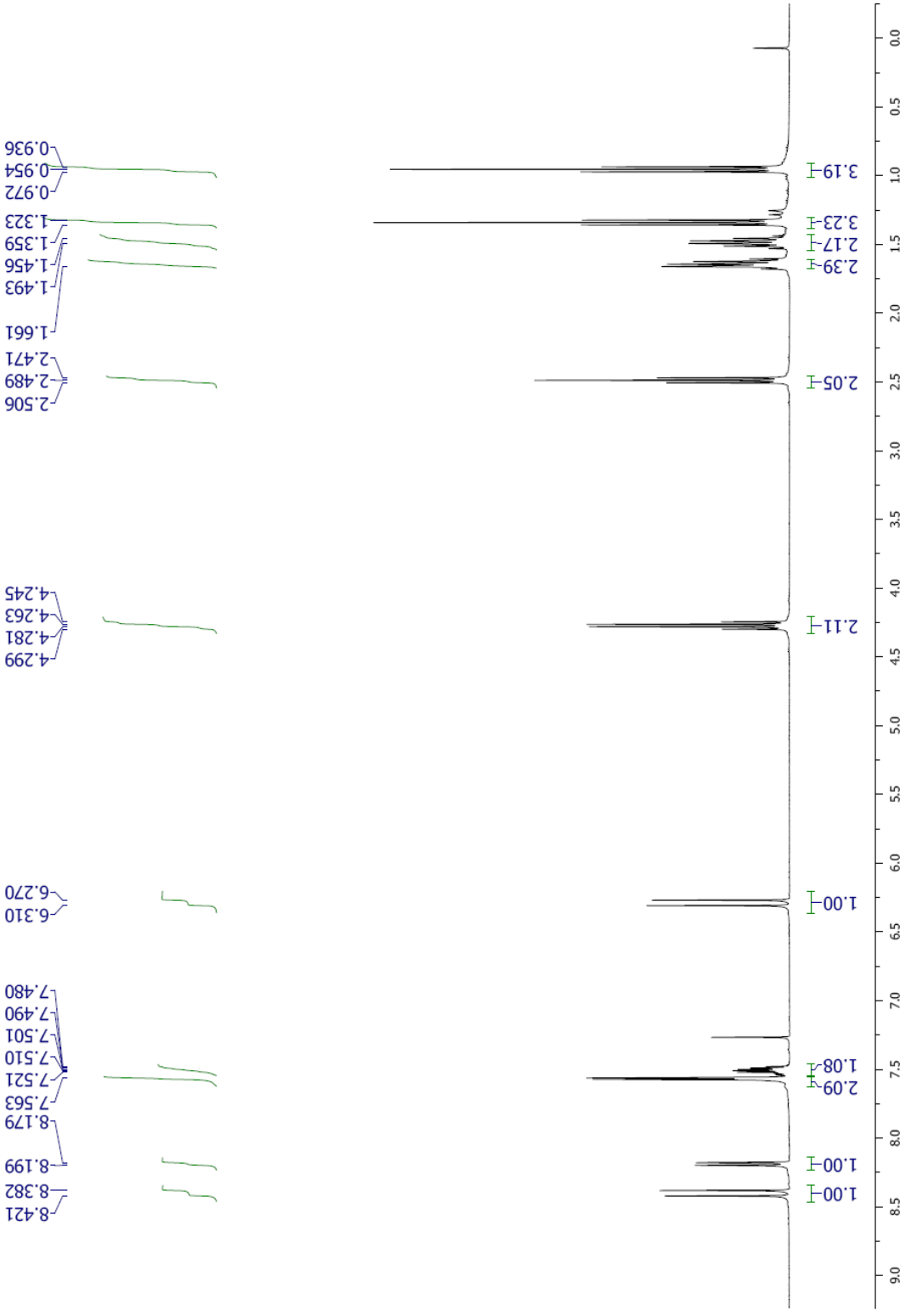
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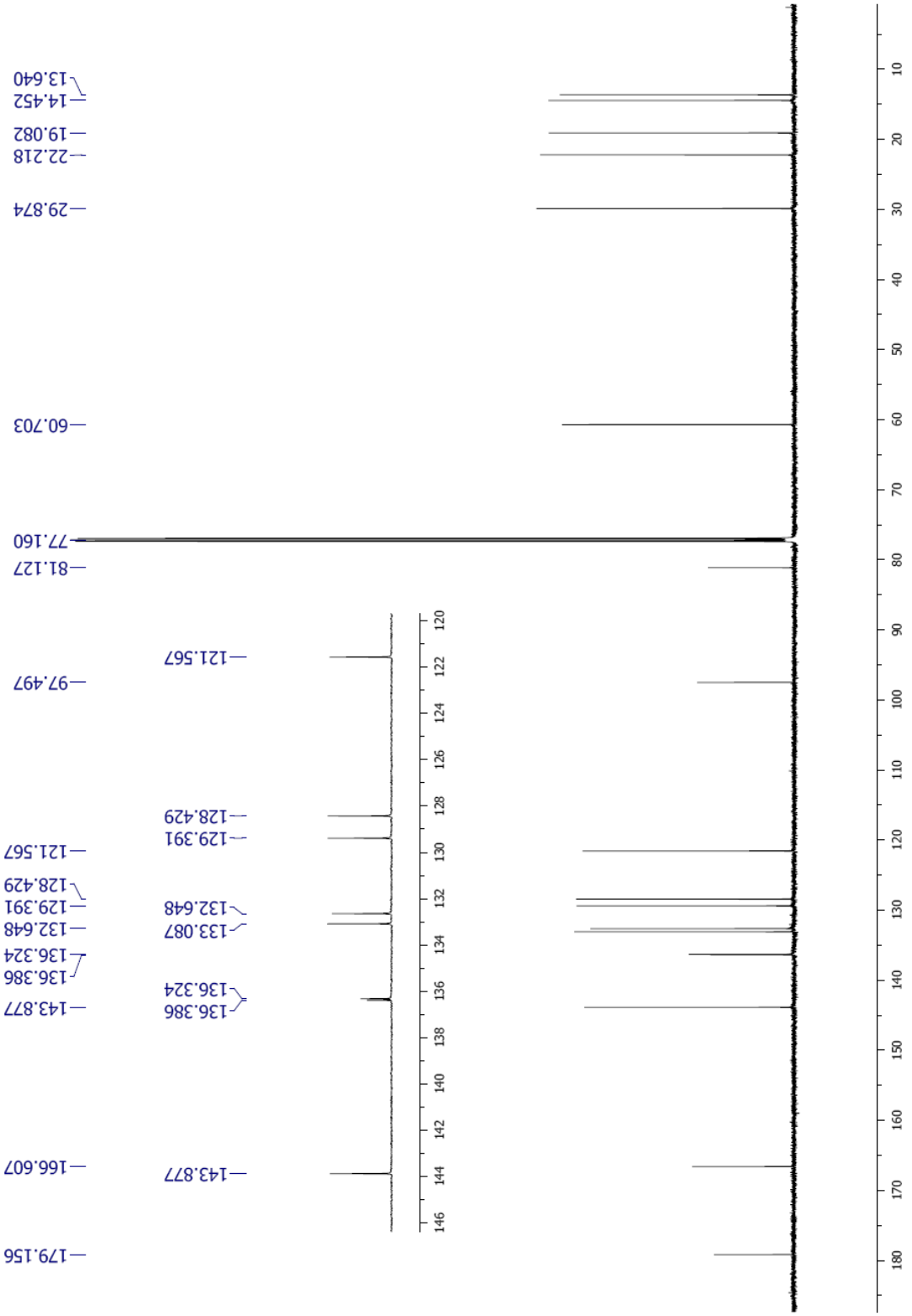
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136.324
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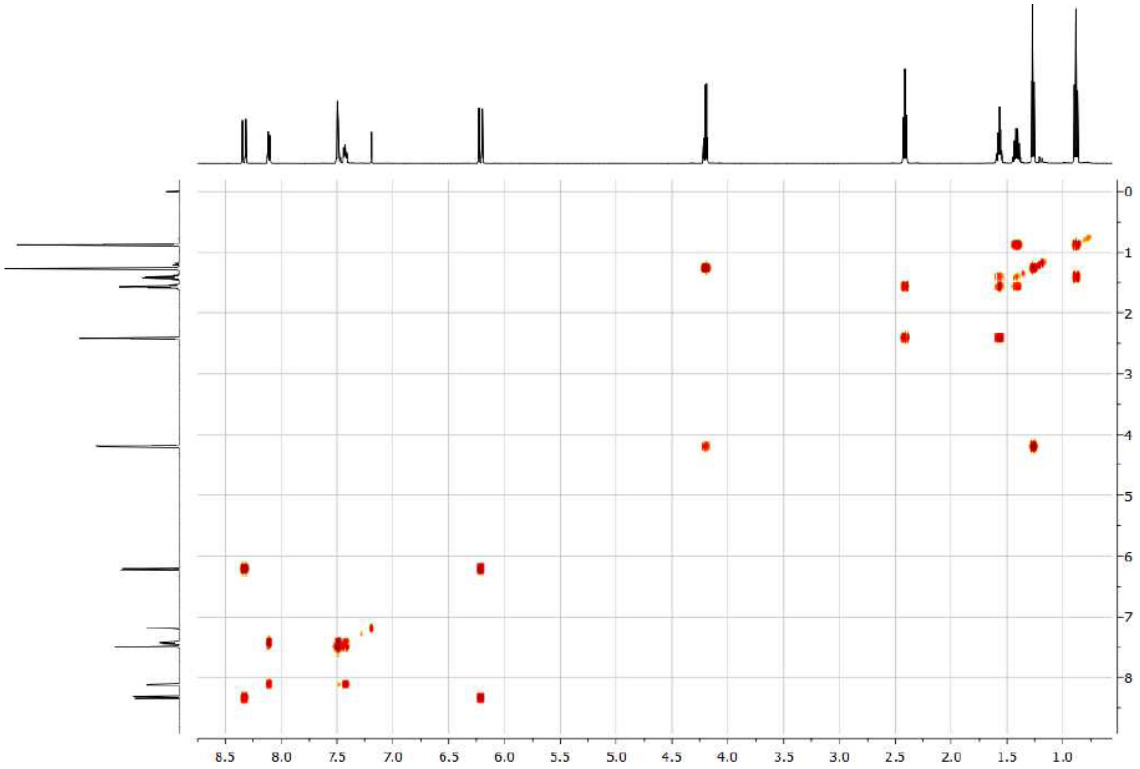
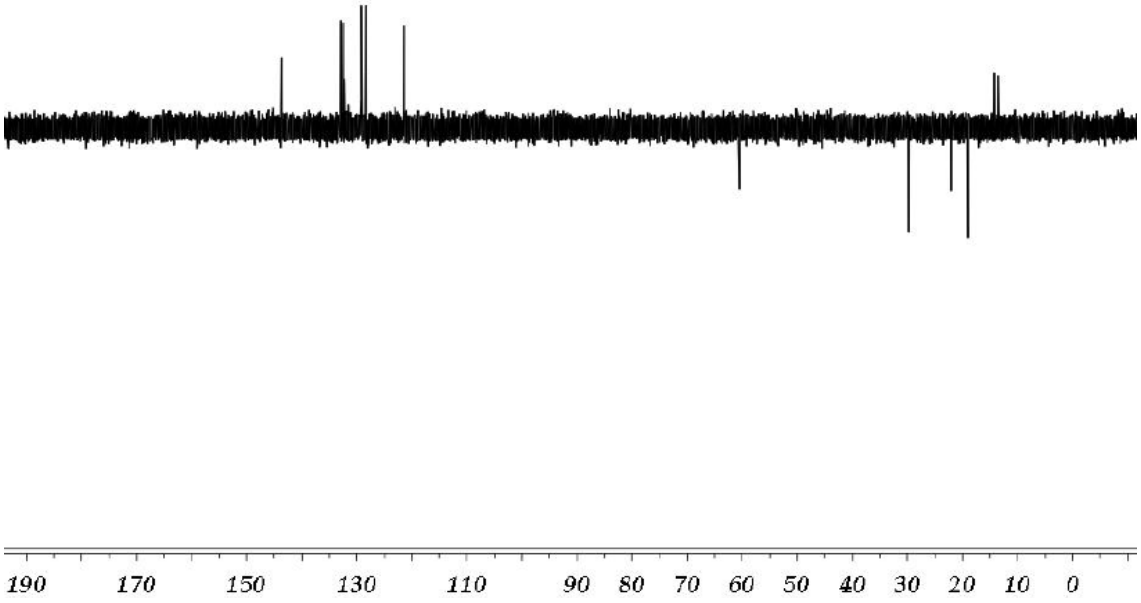
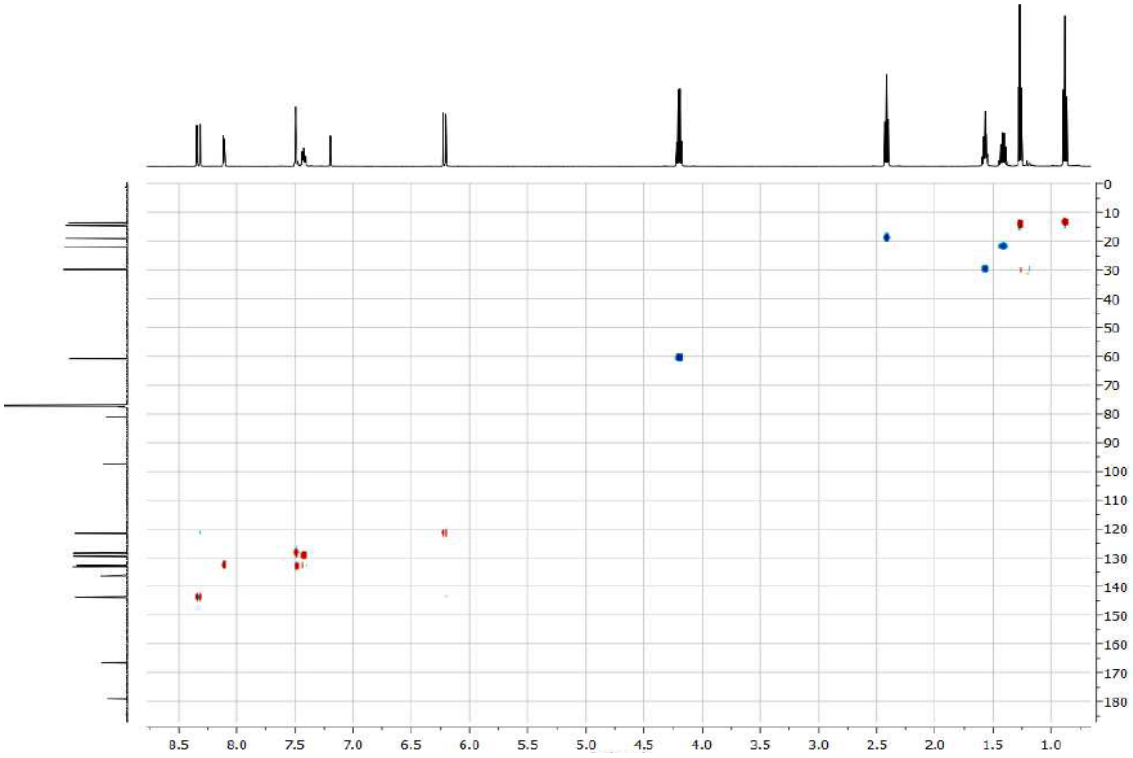
^{1}H COSY (600 MHz)



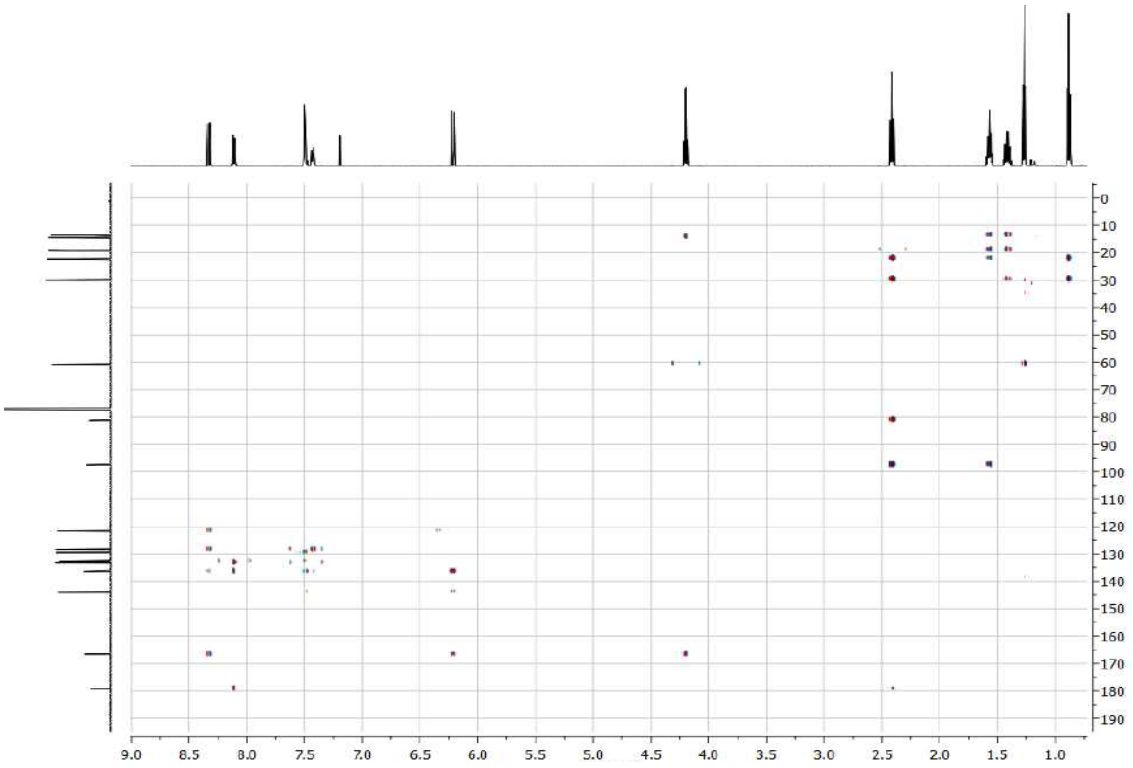
^{13}C DEPT 135 (101 Mhz)

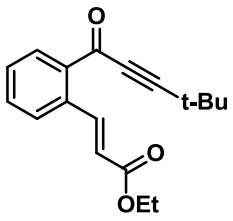


^{1}H-^{13}C HSQC (600 MHz)



^{1}H-^{13}C HMBC (600 MHz)

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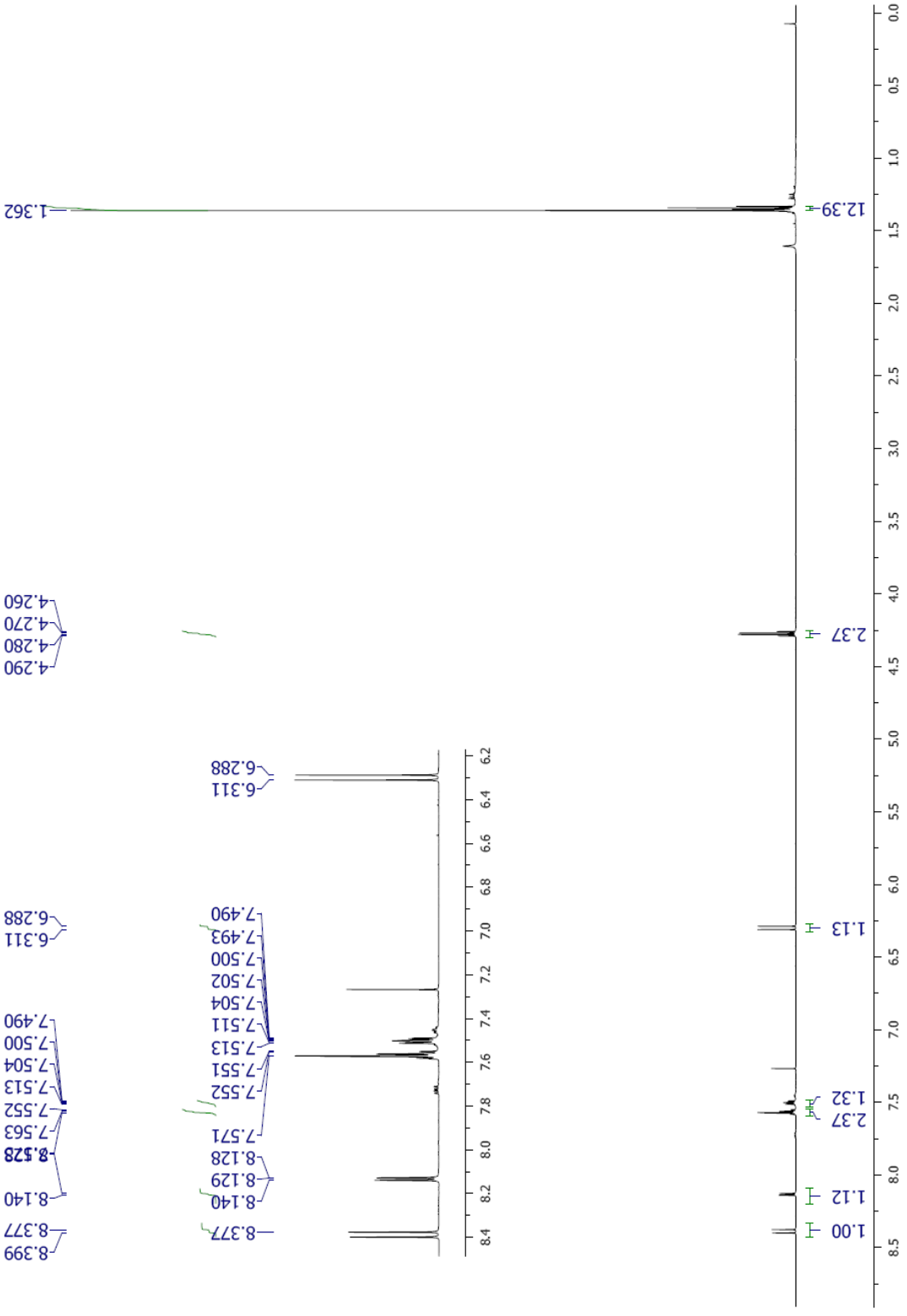
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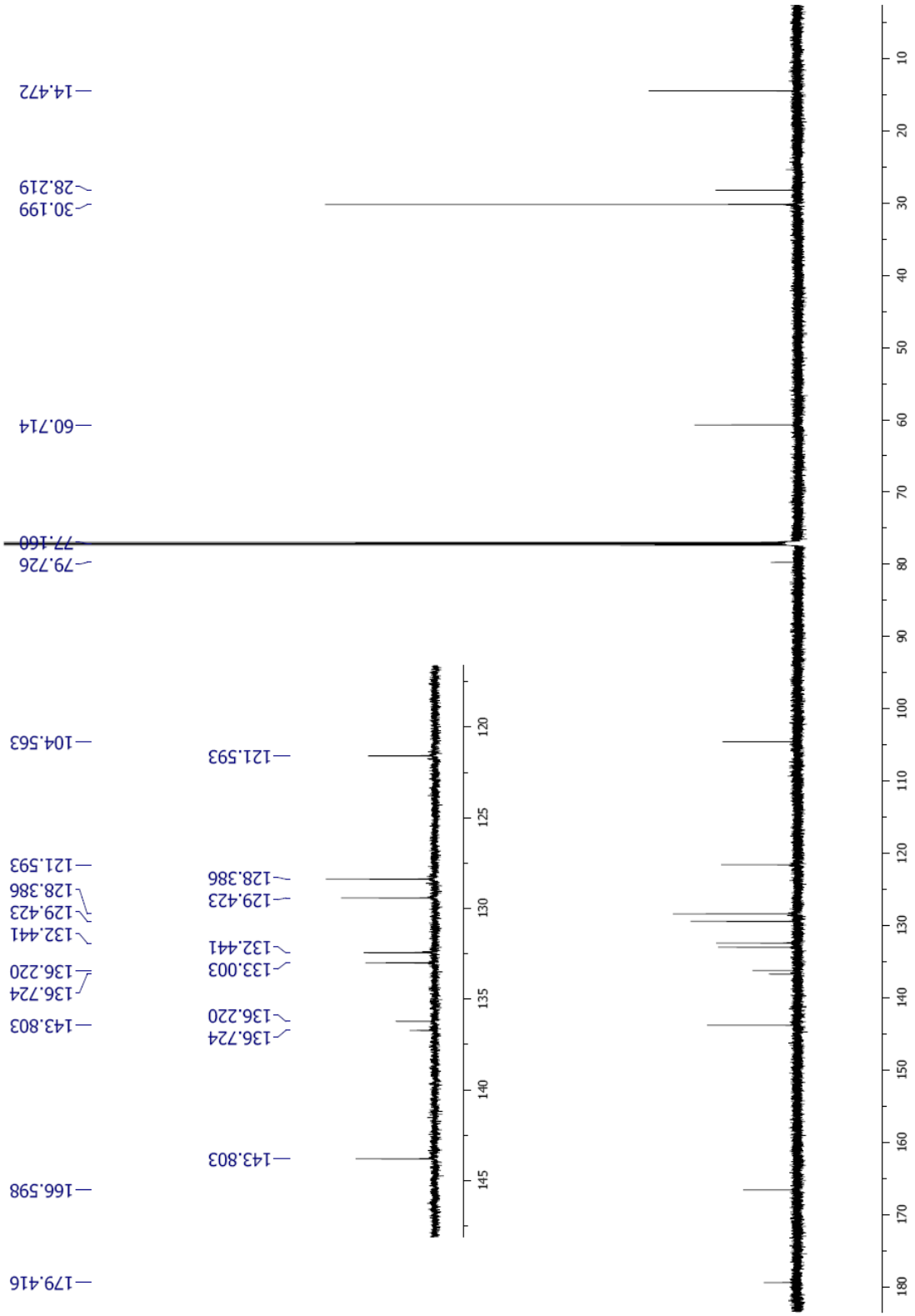
6.288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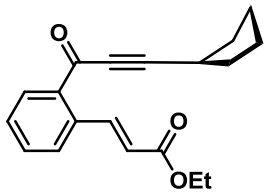
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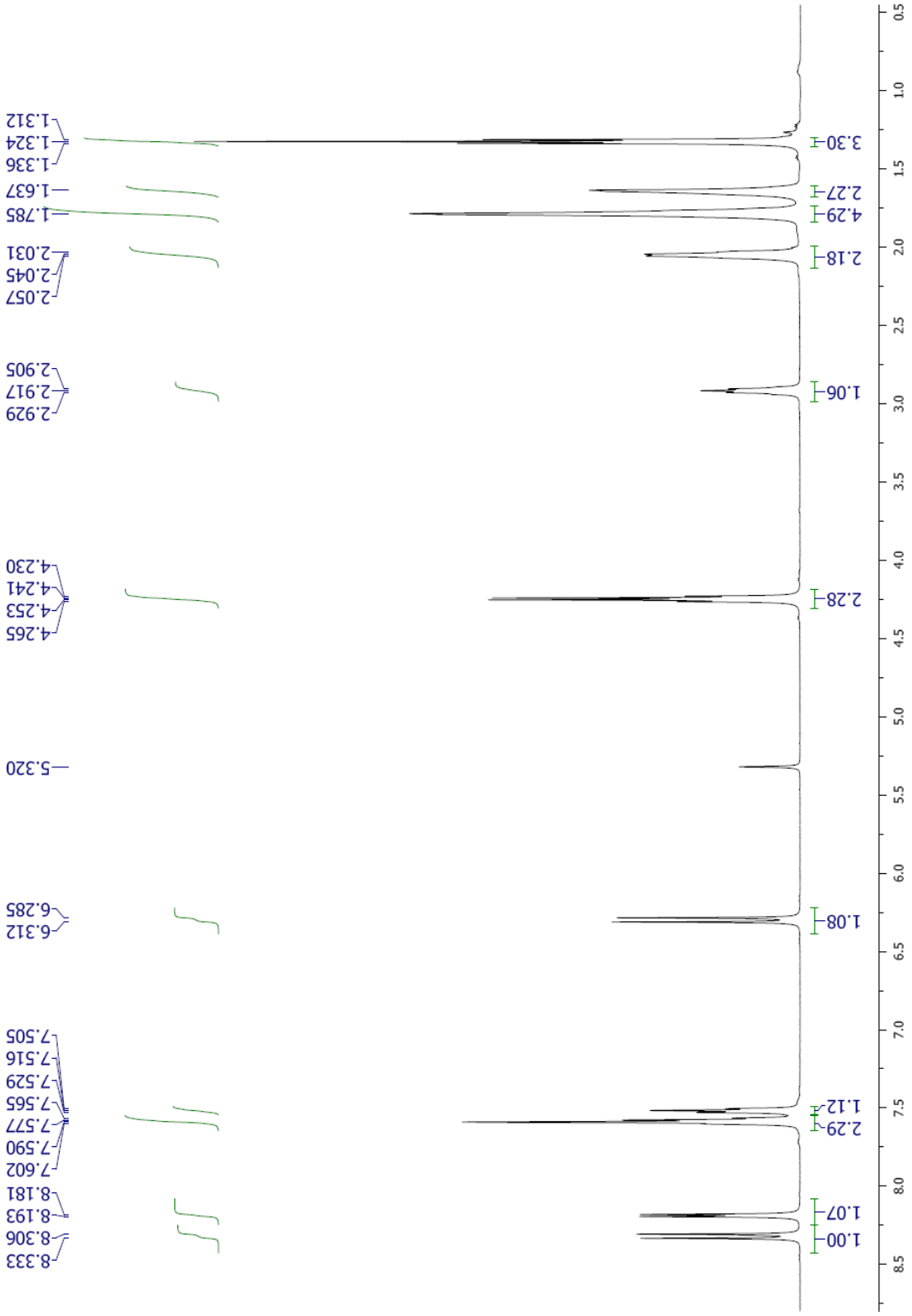
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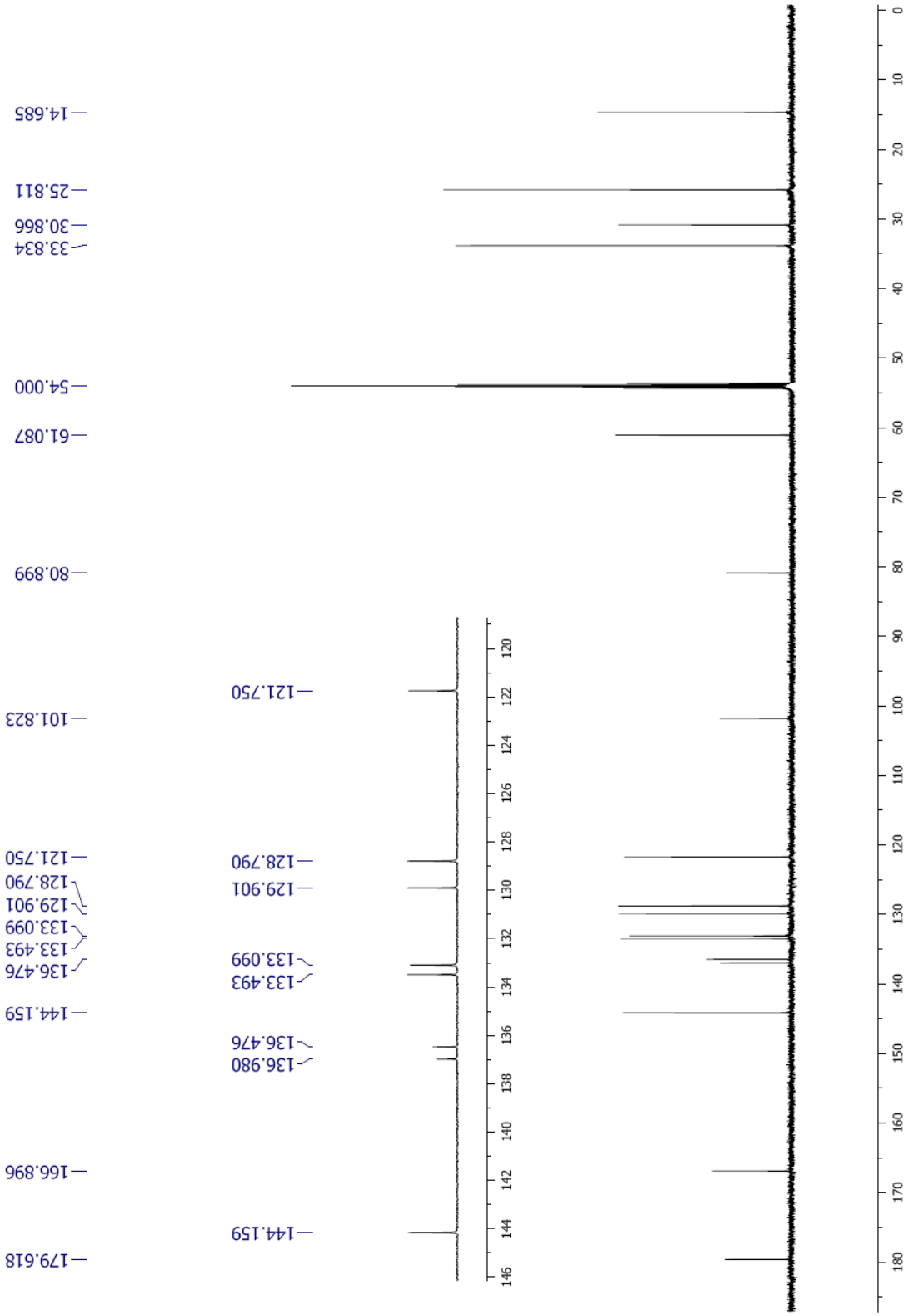
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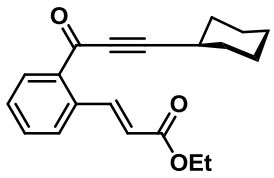
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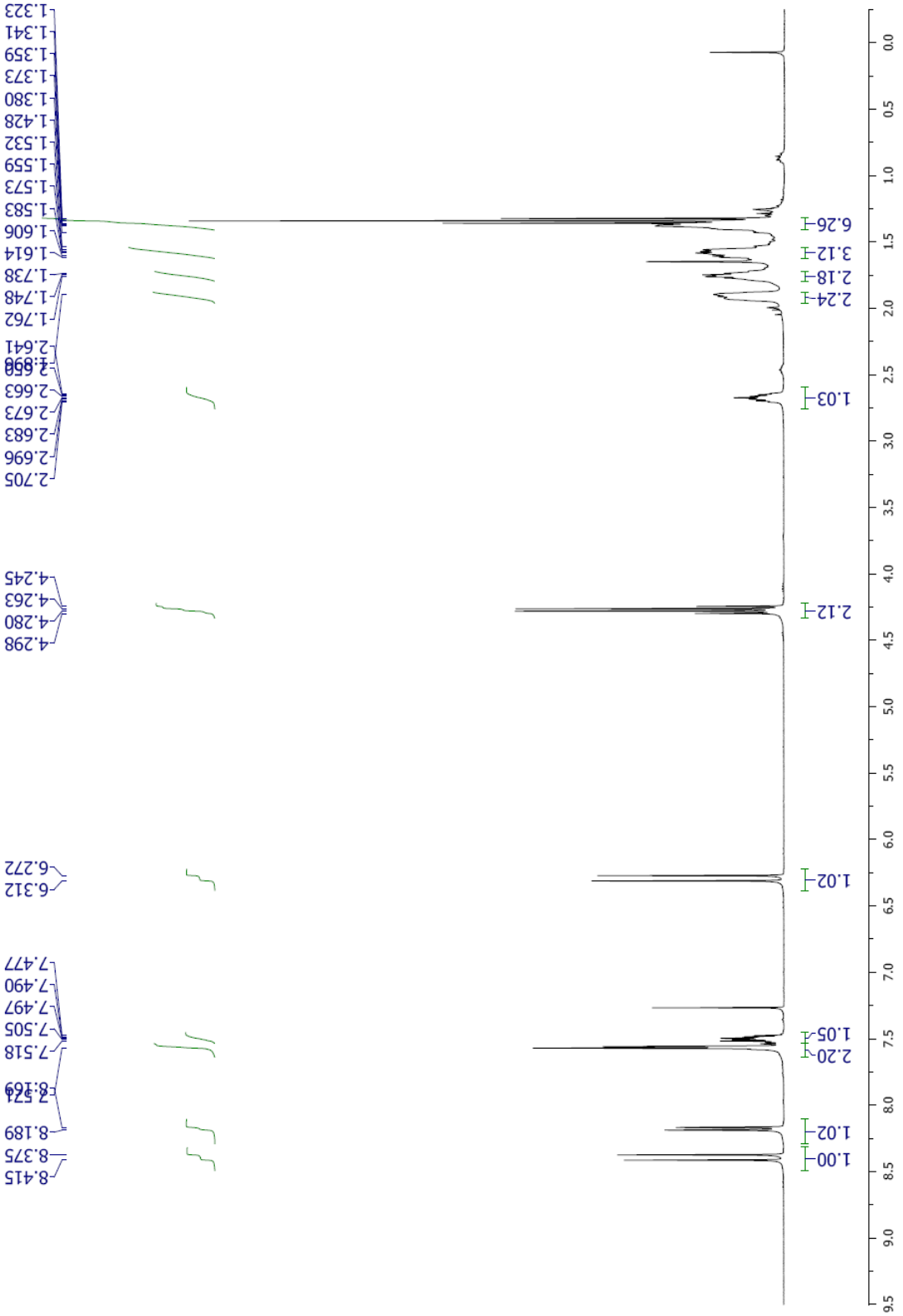
O
OEt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3.12
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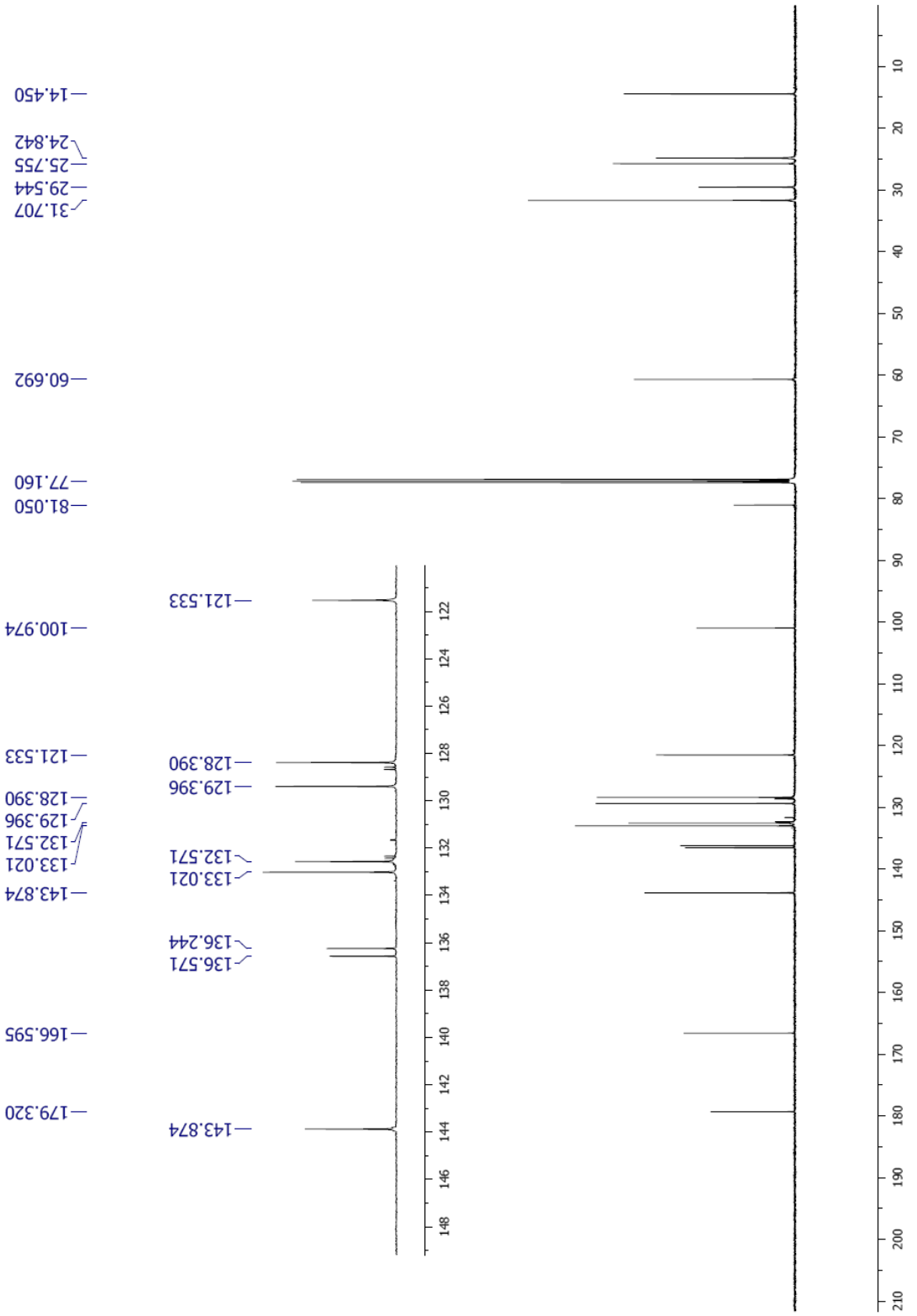

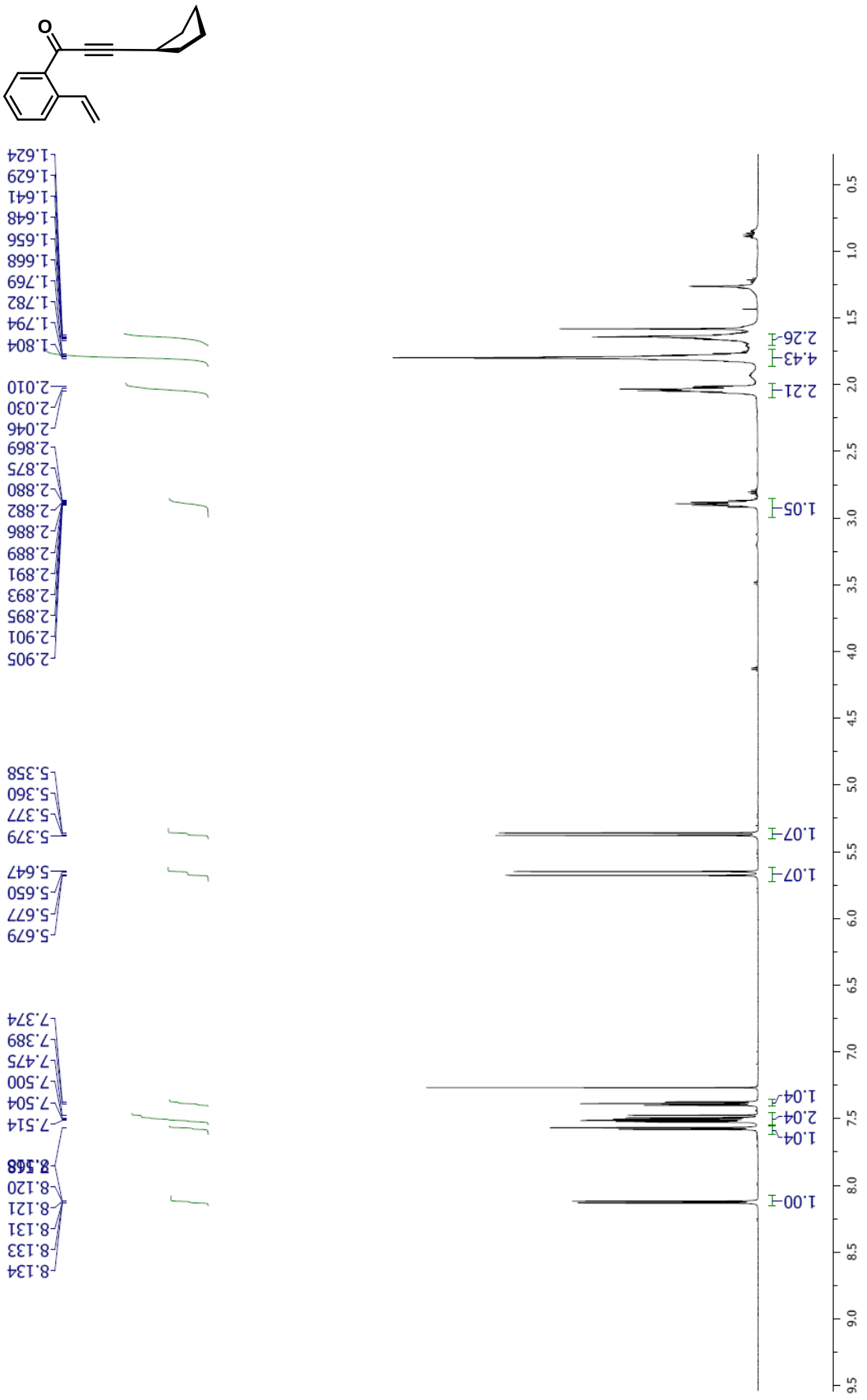
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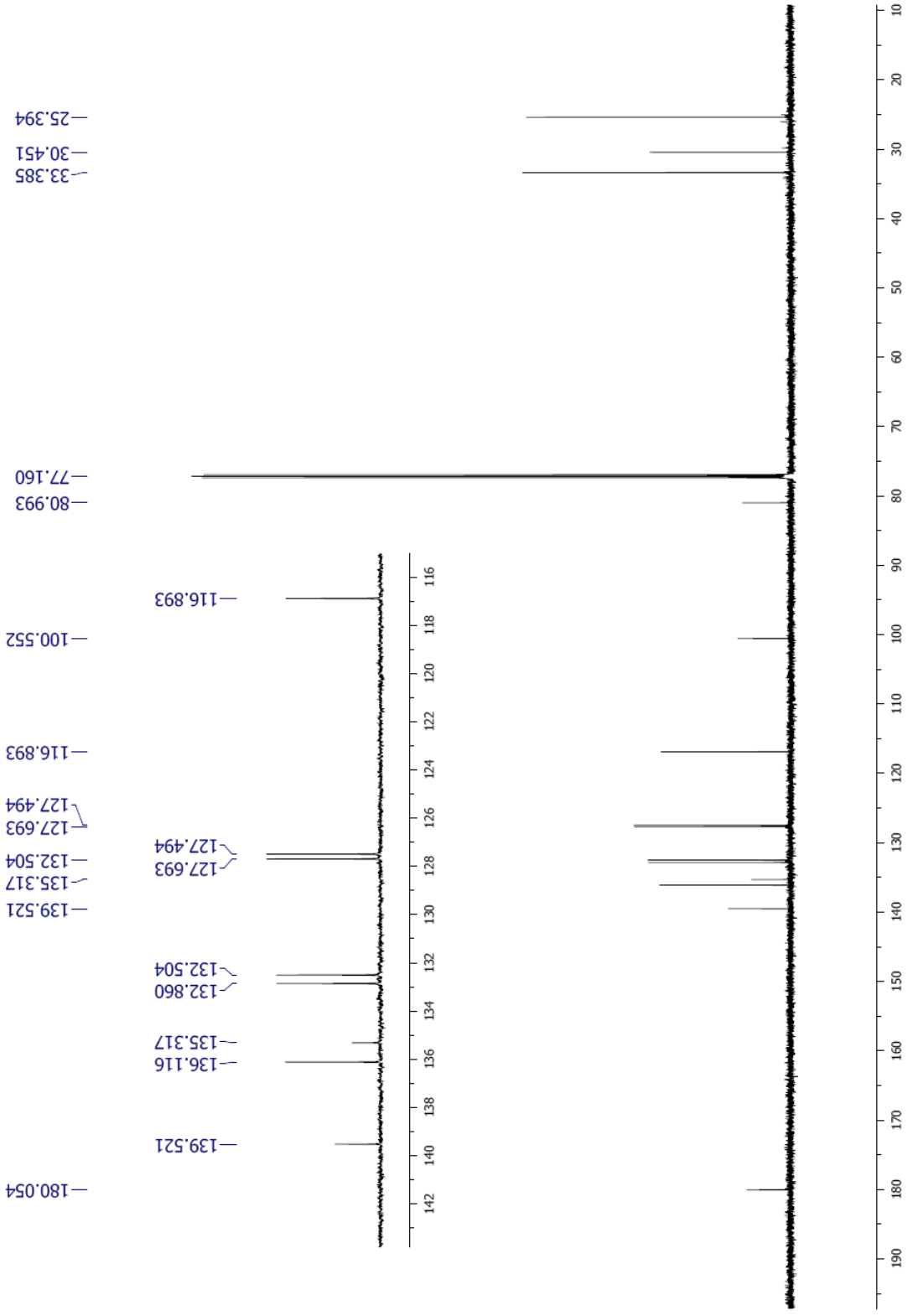
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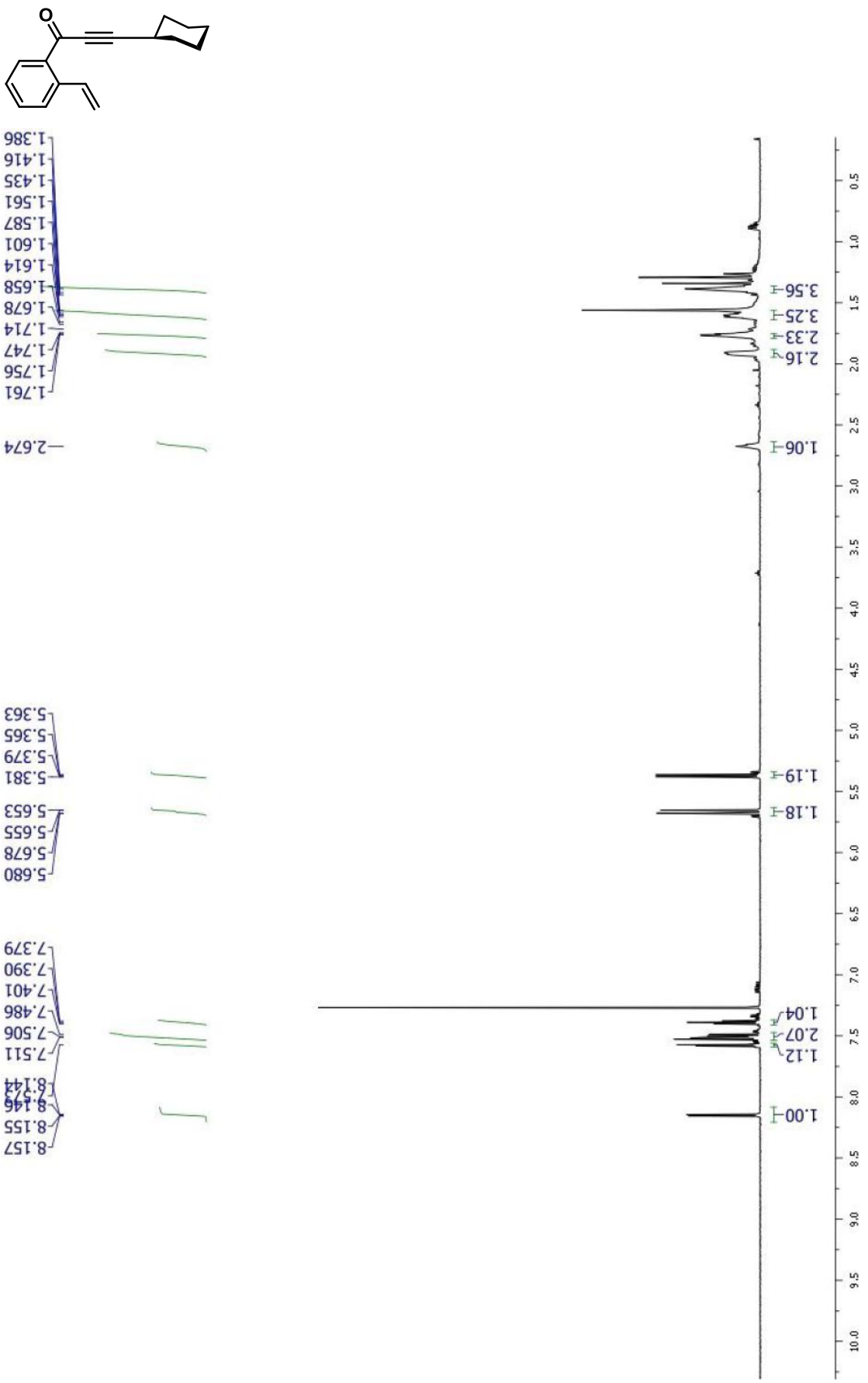
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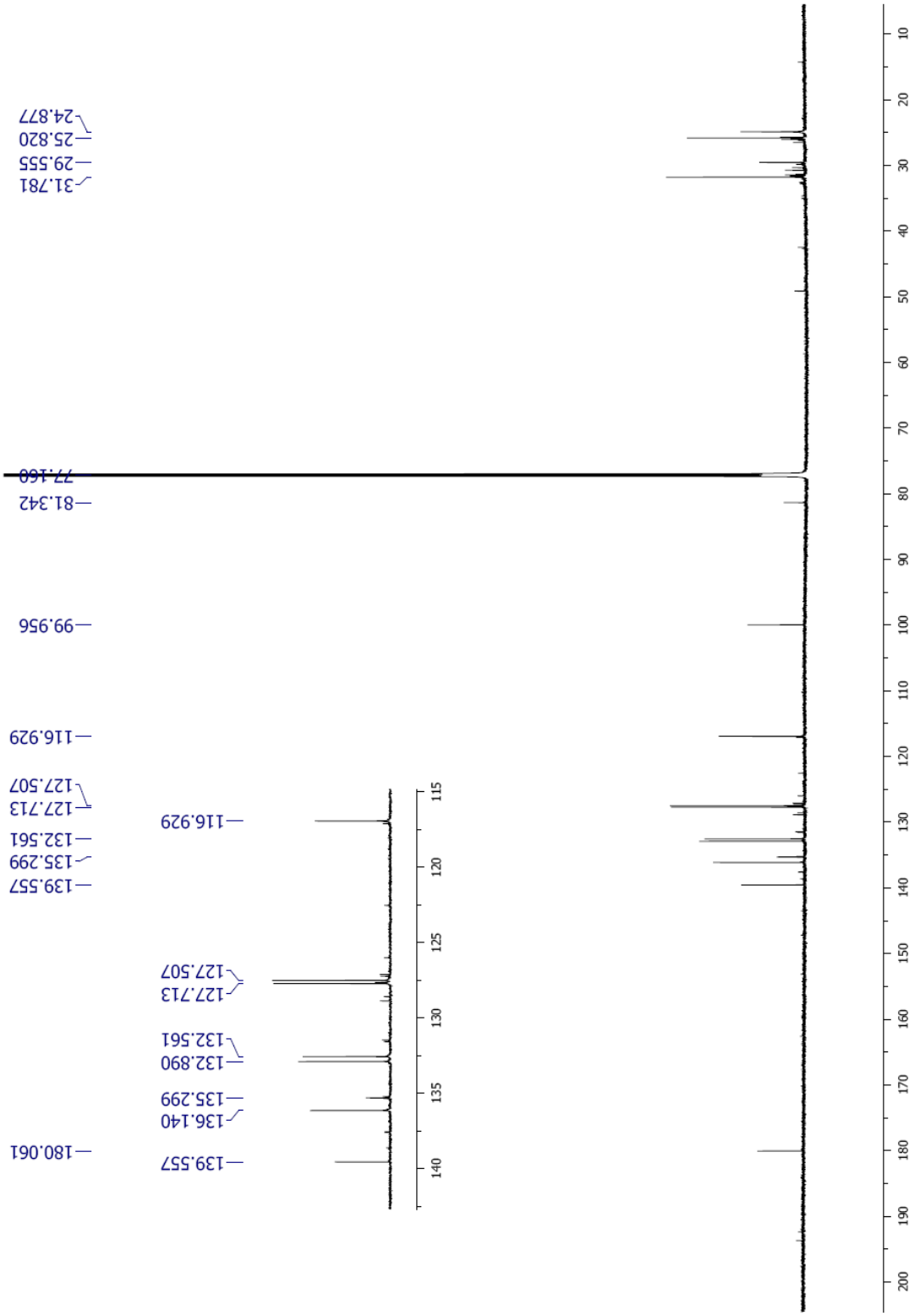

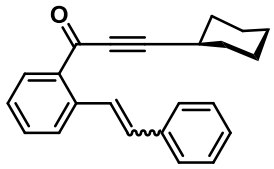

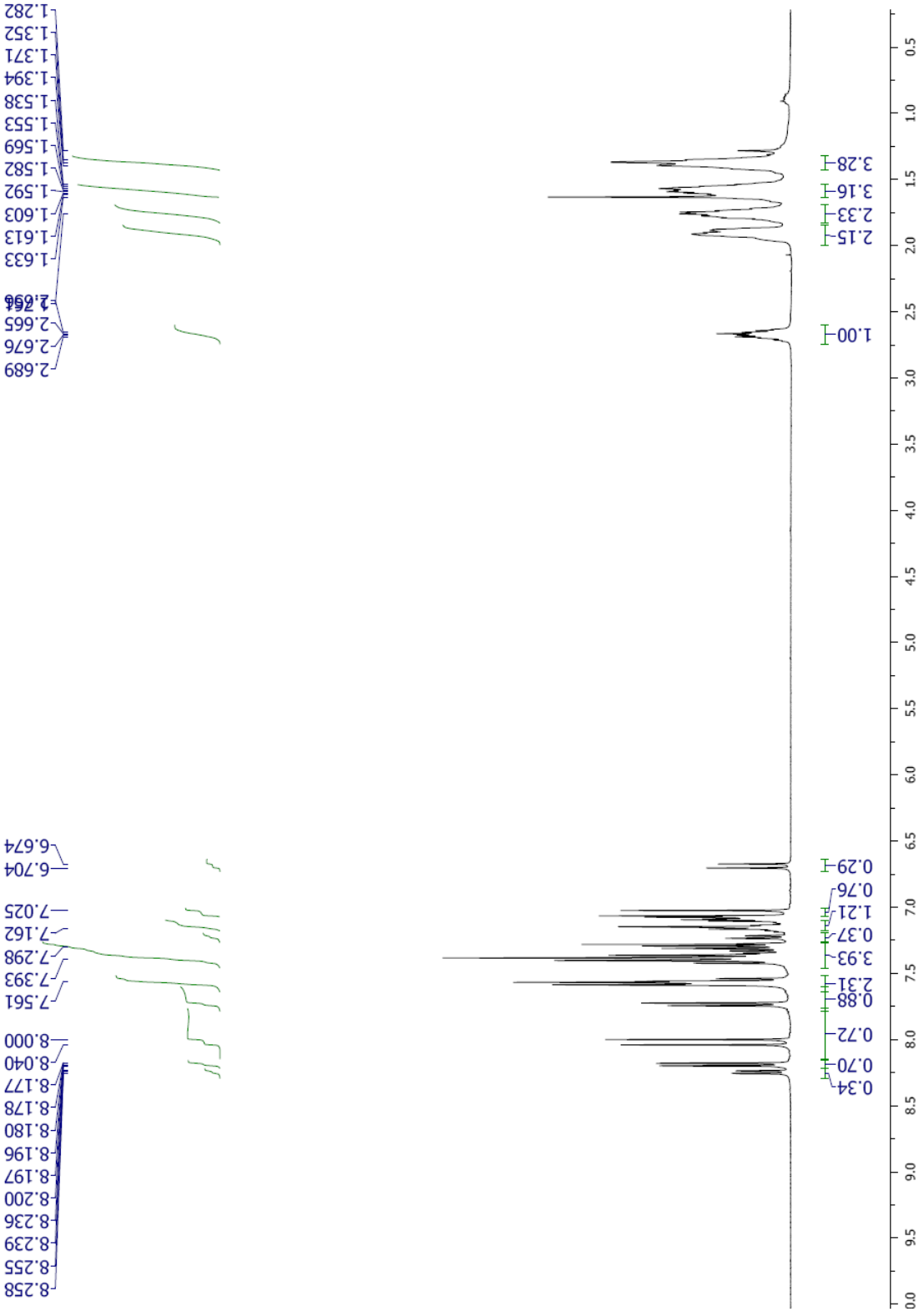
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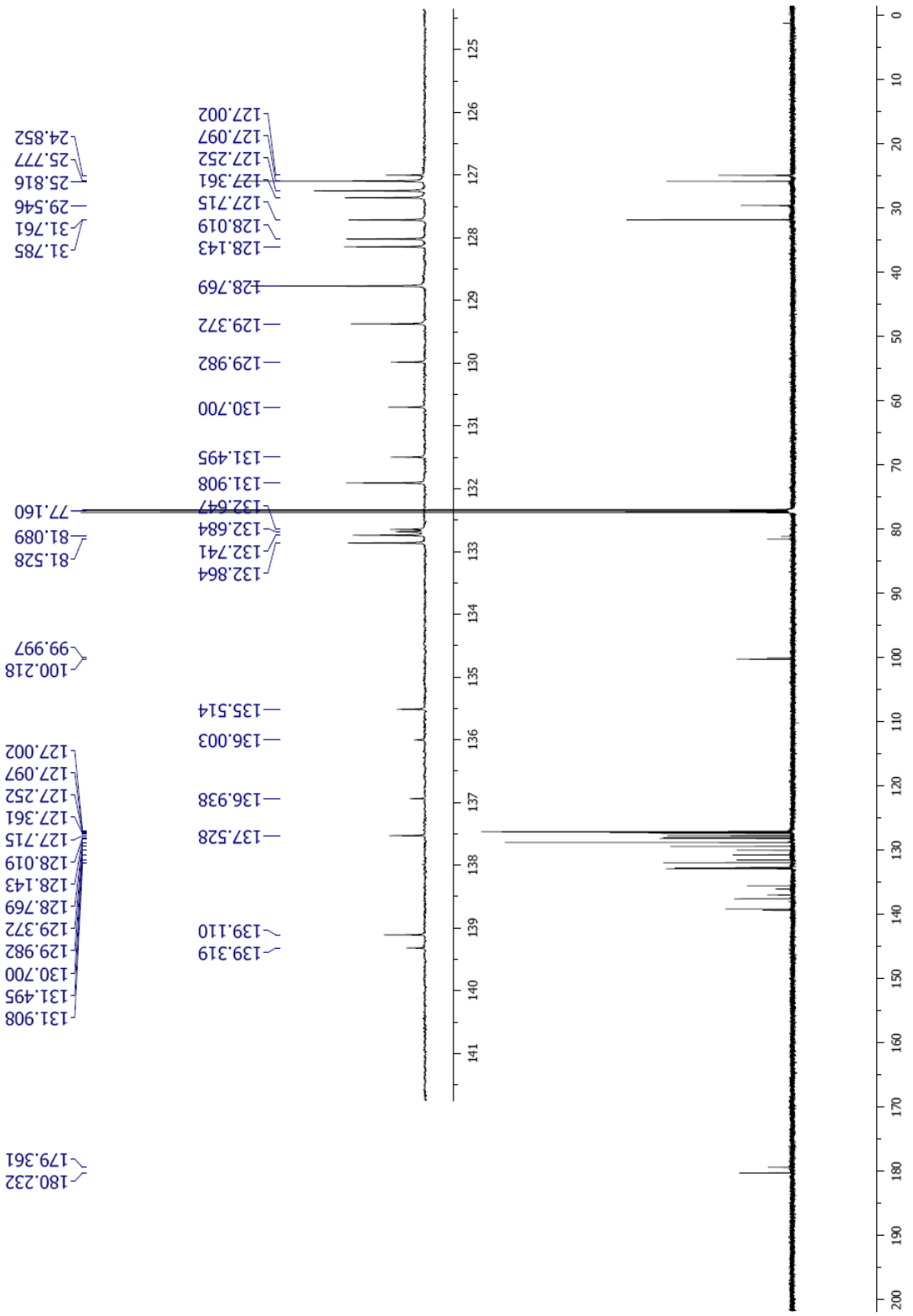
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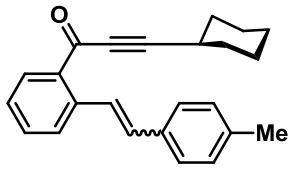
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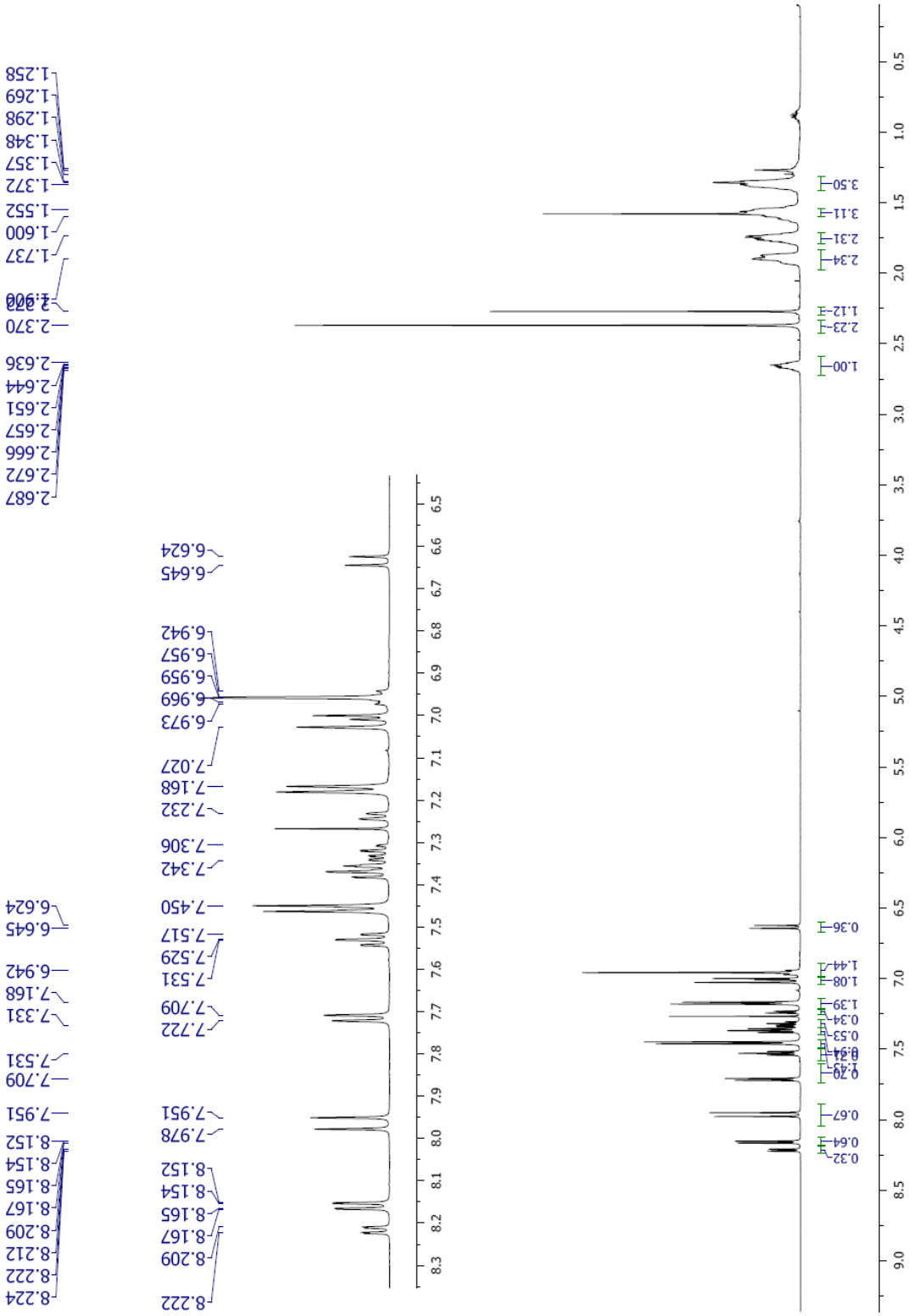

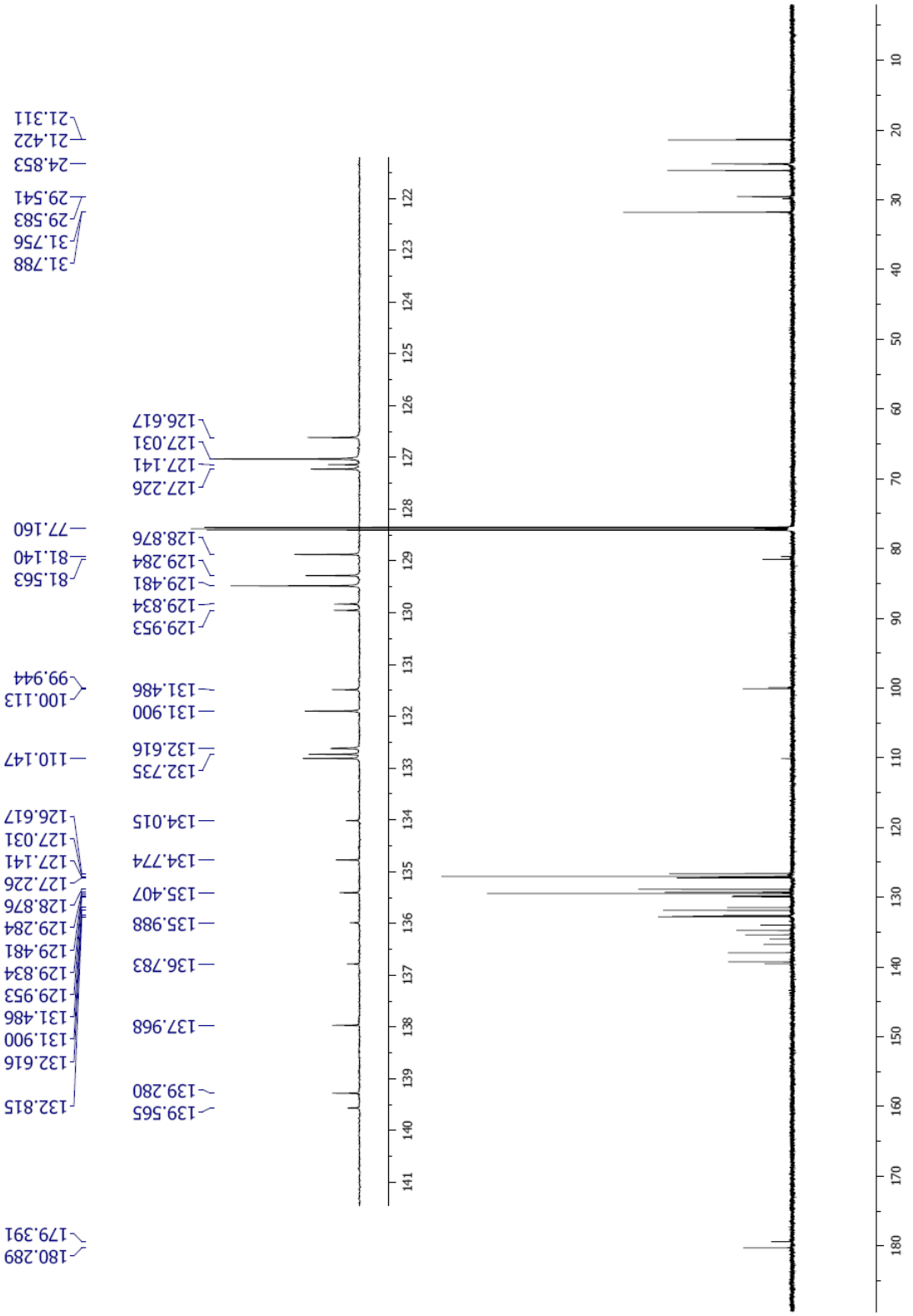
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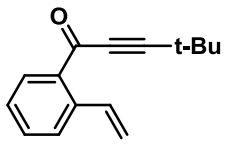
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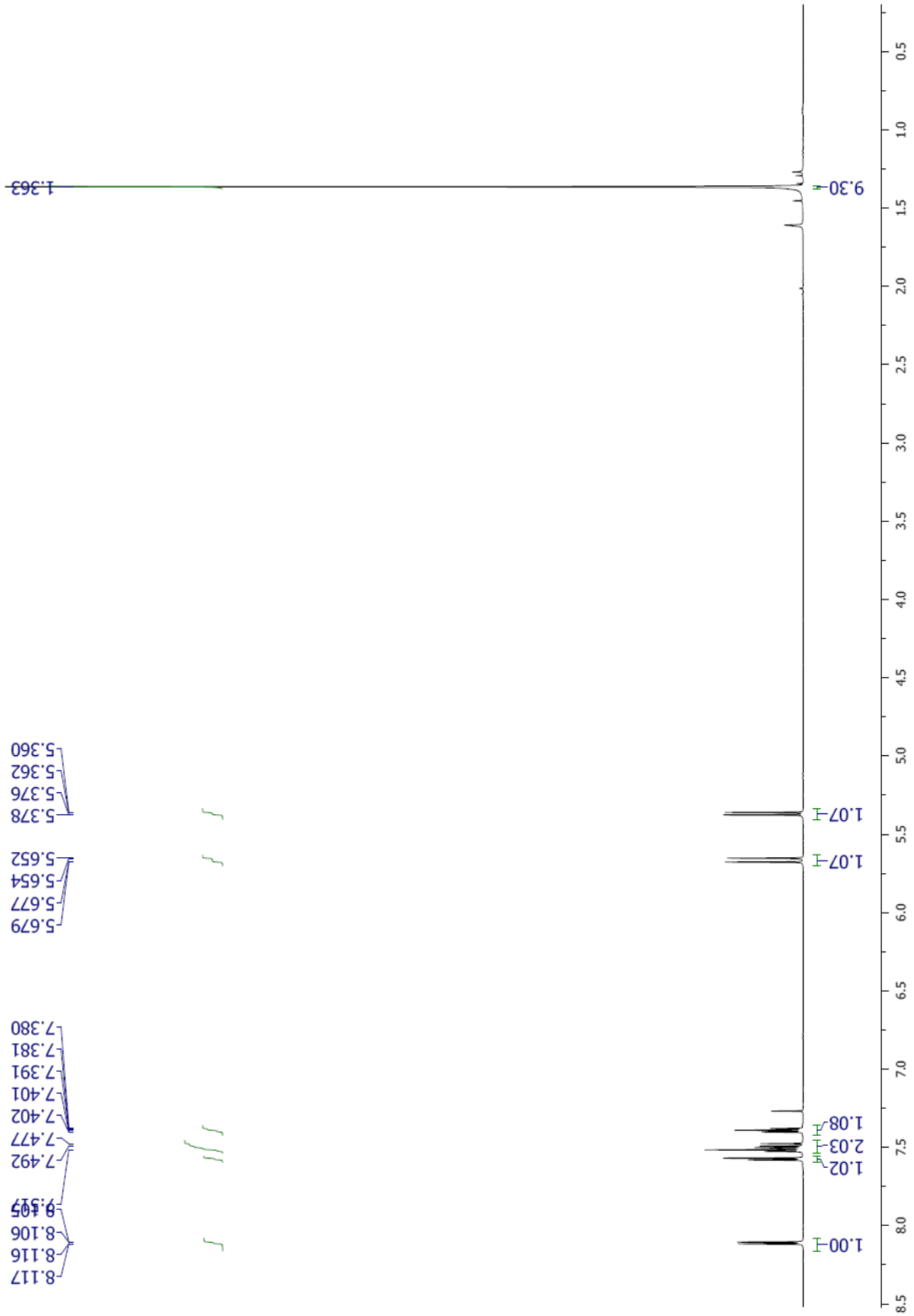
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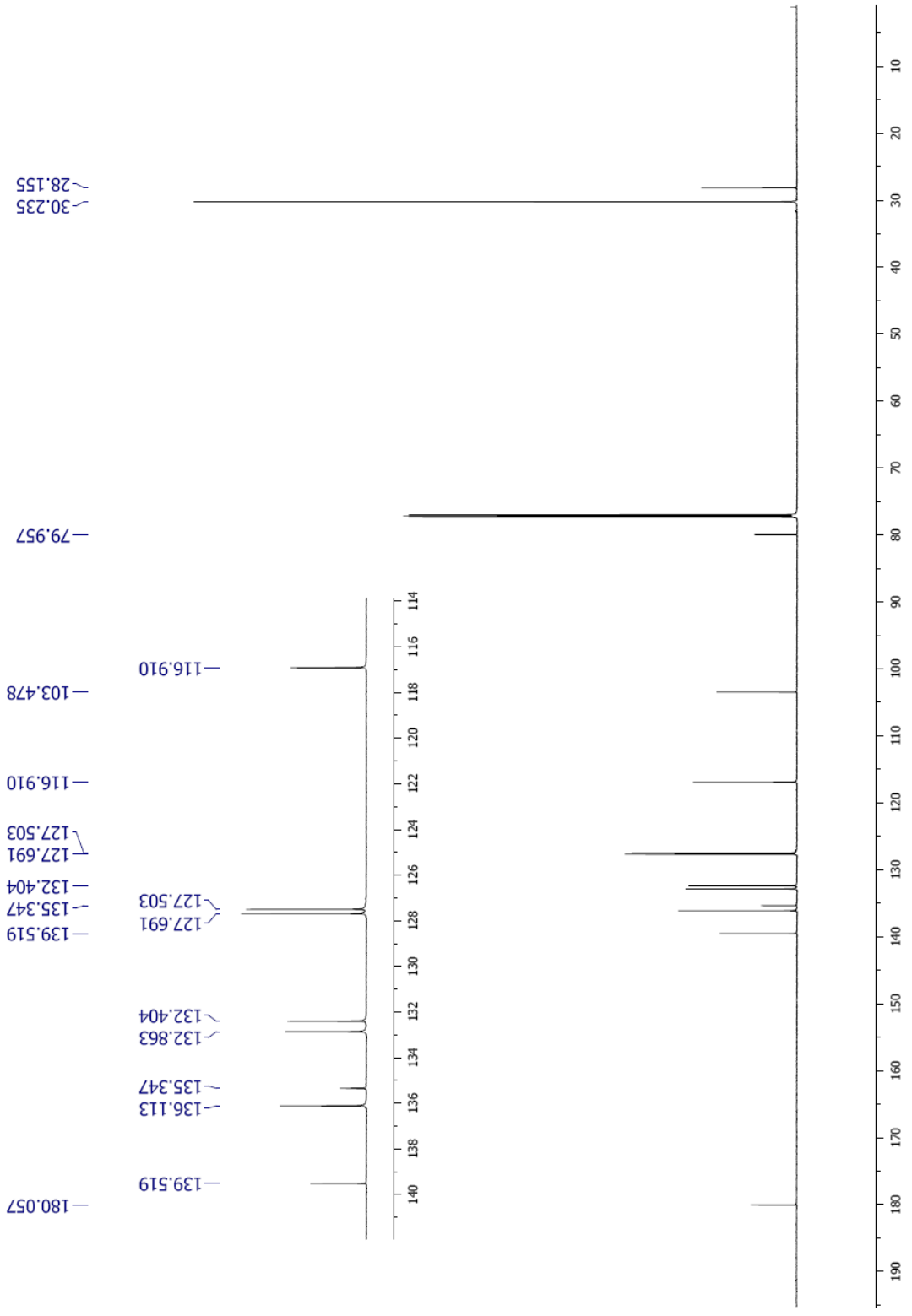

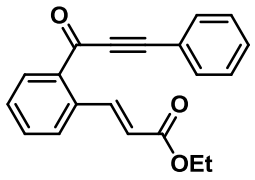
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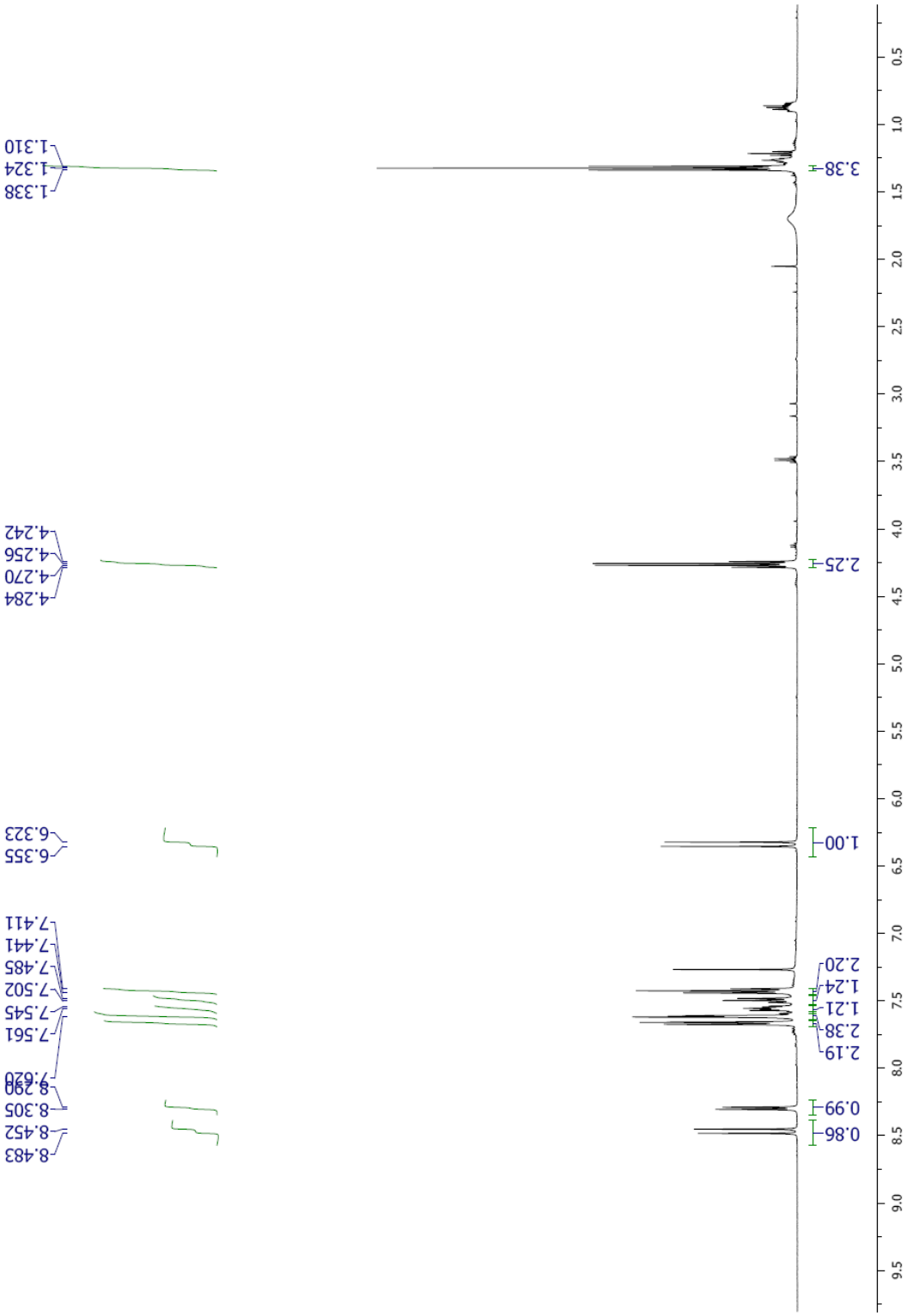
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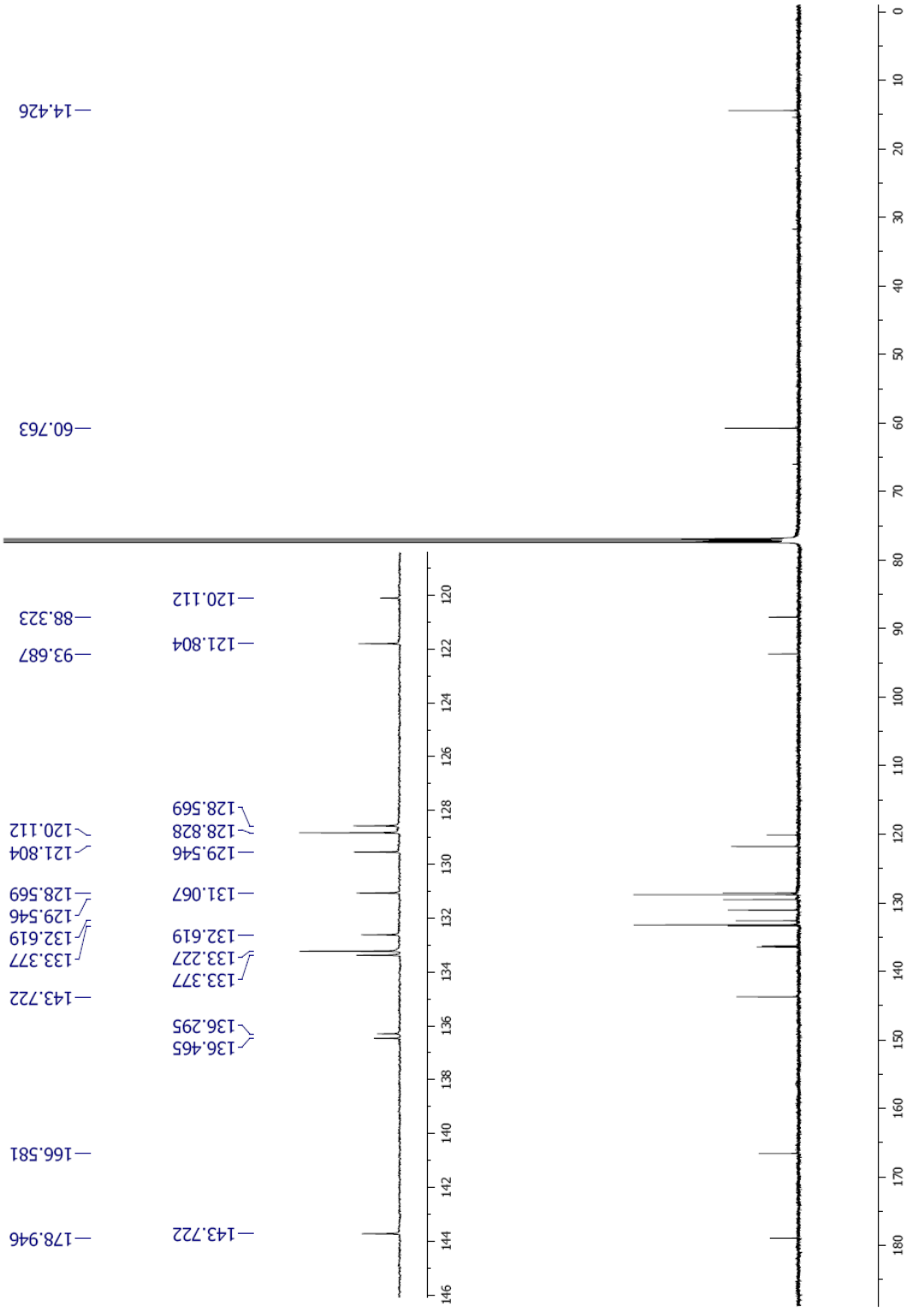
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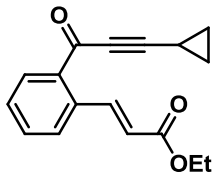
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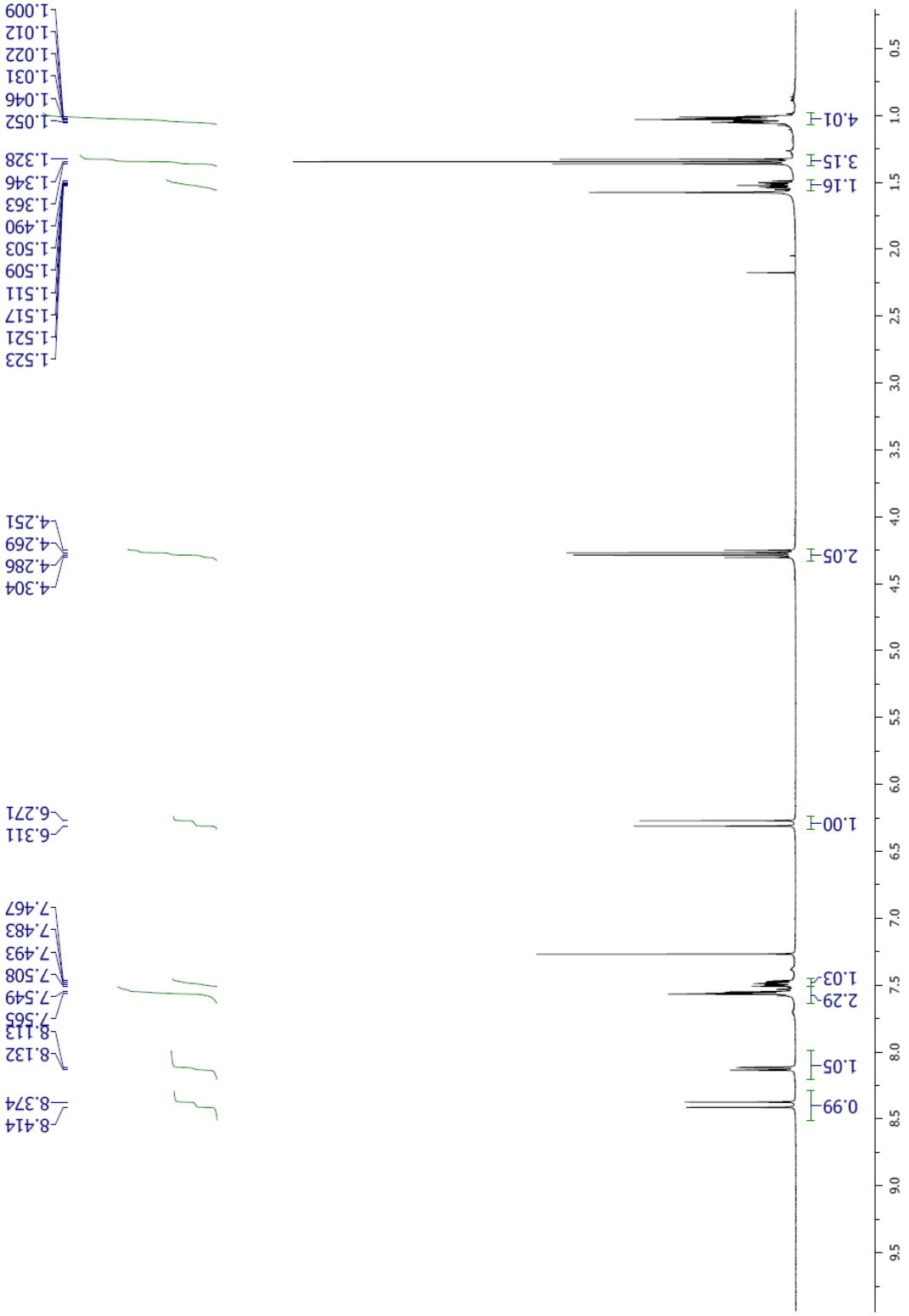
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1.521
1.523
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4.286
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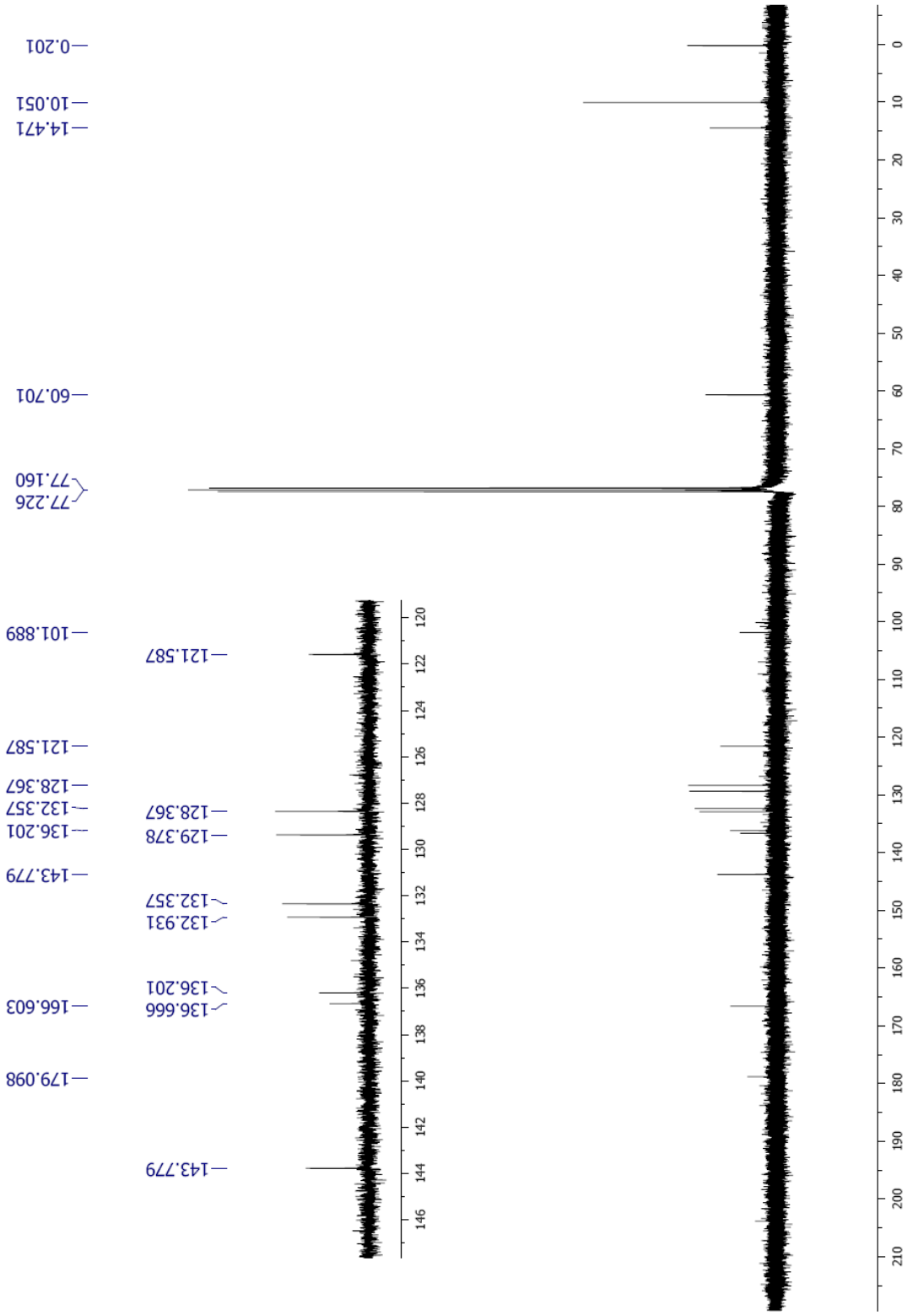
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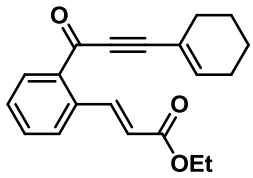
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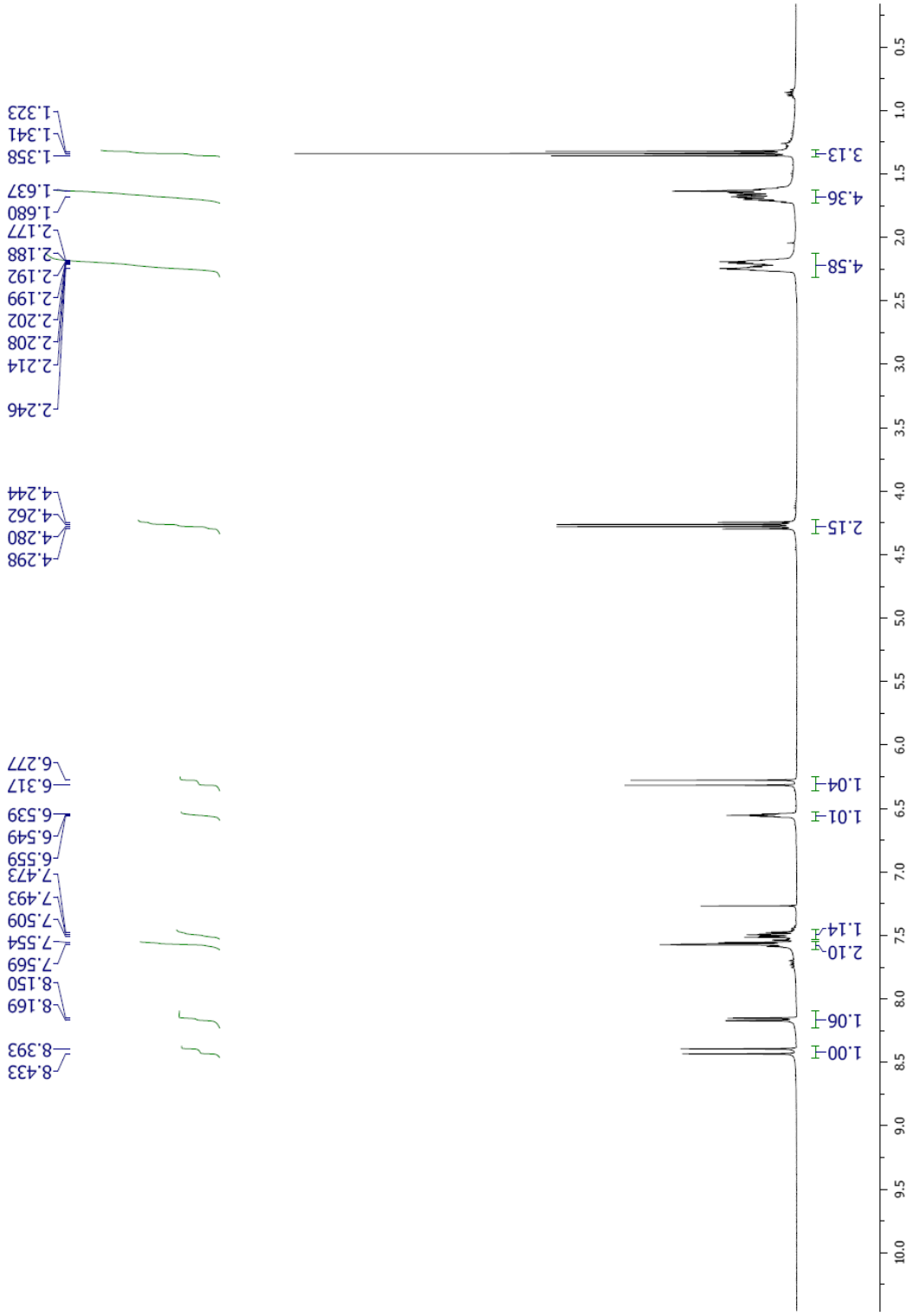
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4.262
4.280
4.298
6.277
6.317
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6.549
6.559
7.473
7.493
7.509
7.554
7.569
8.150
8.169
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1.01
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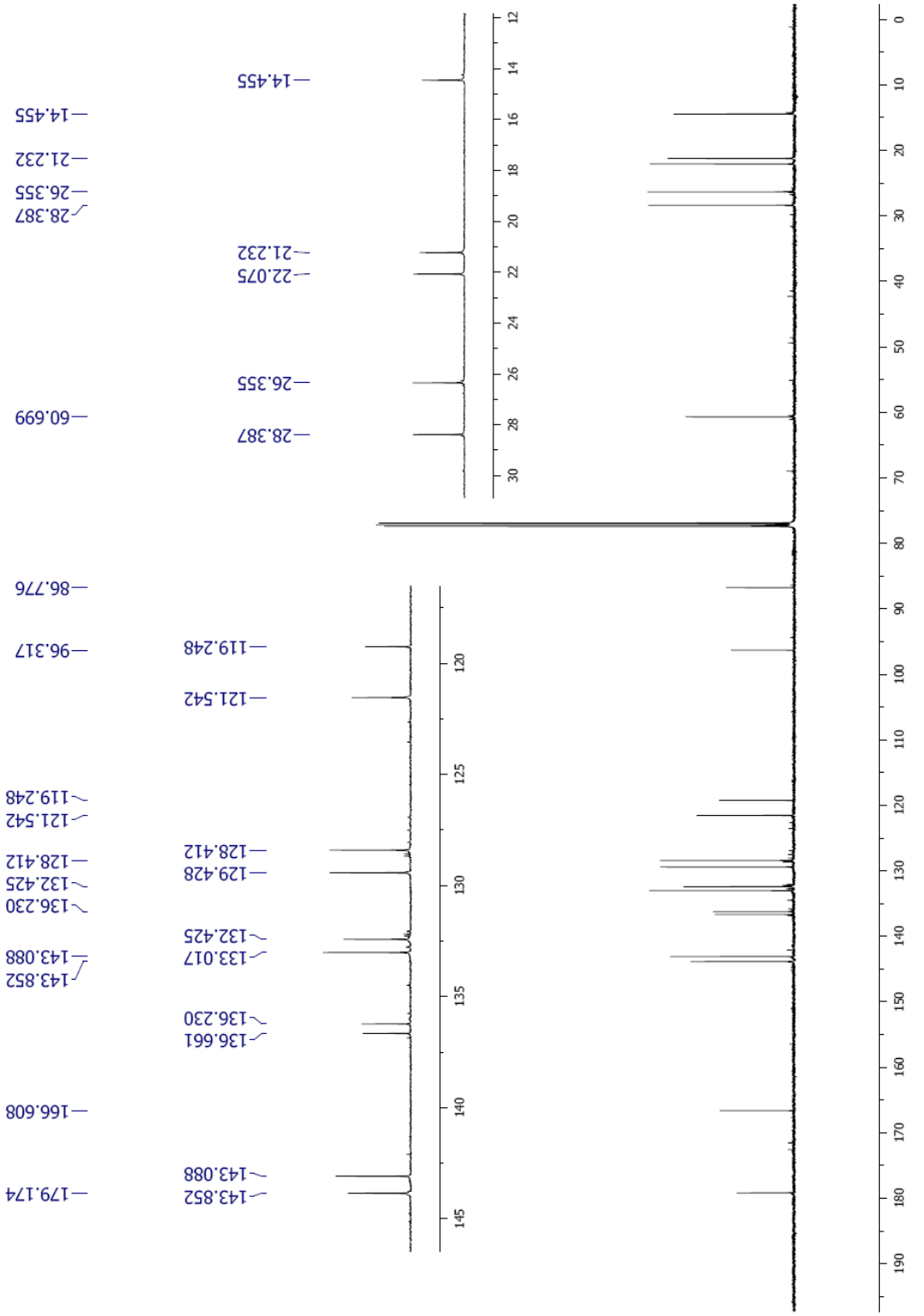
1.00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119.248
121.542
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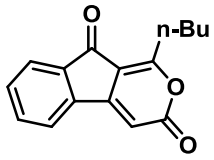
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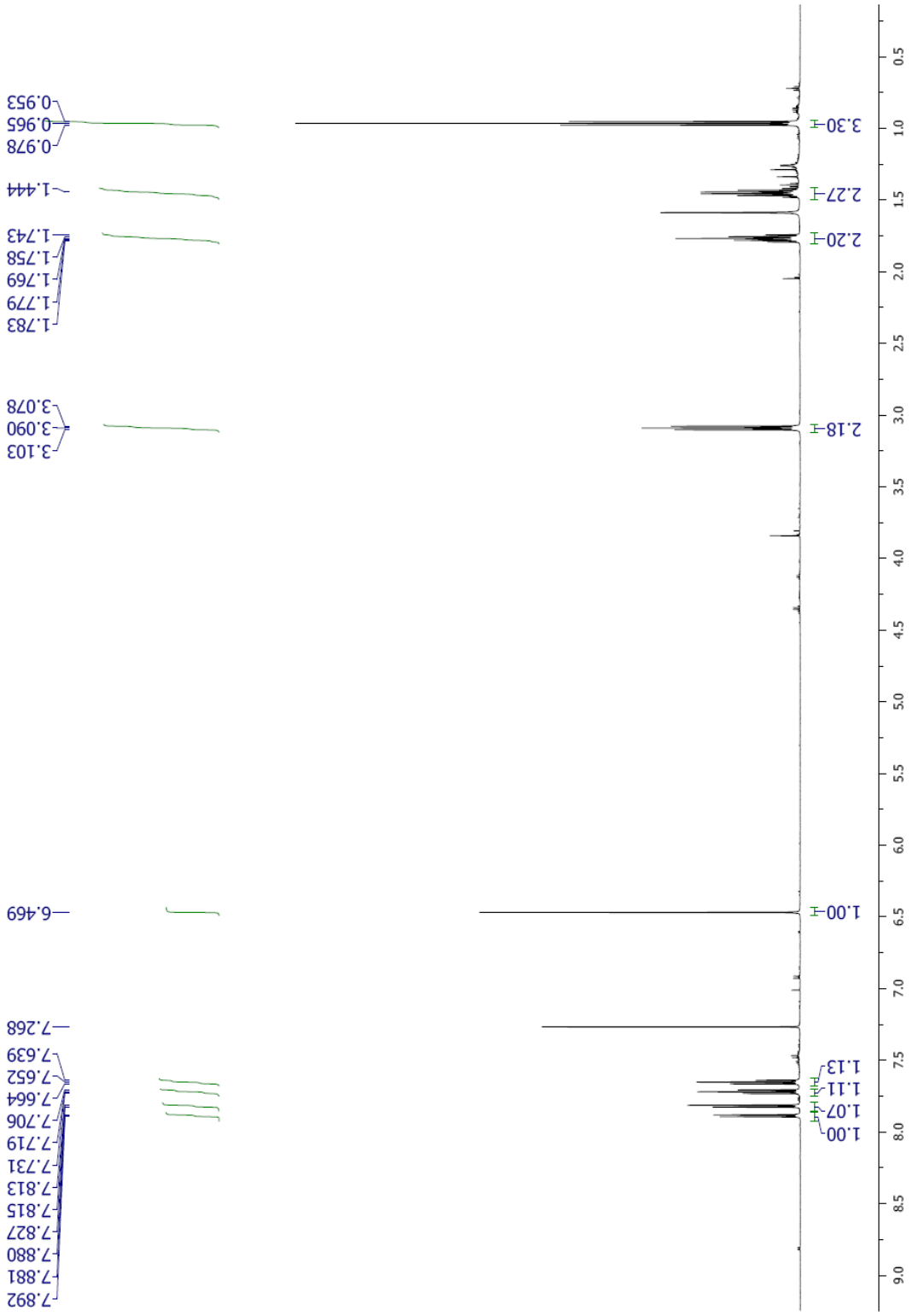
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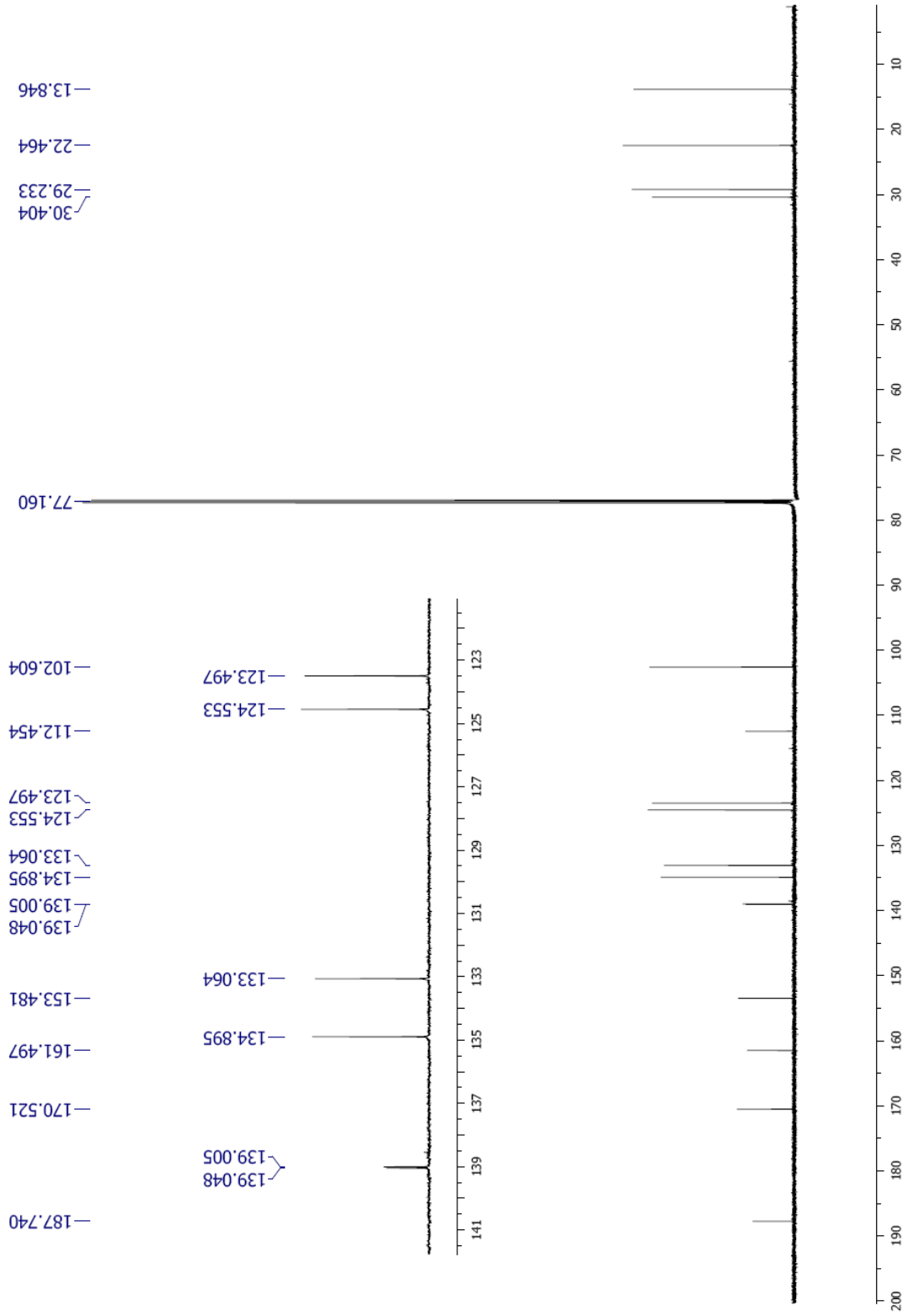
1.00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123.497
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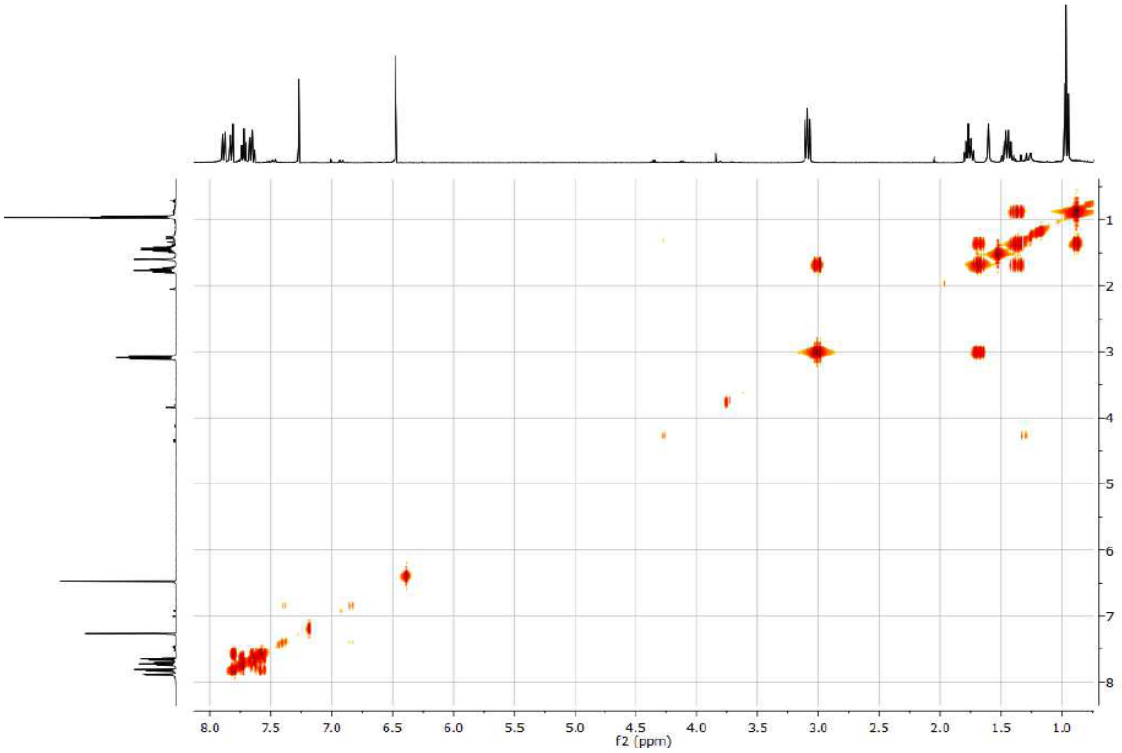
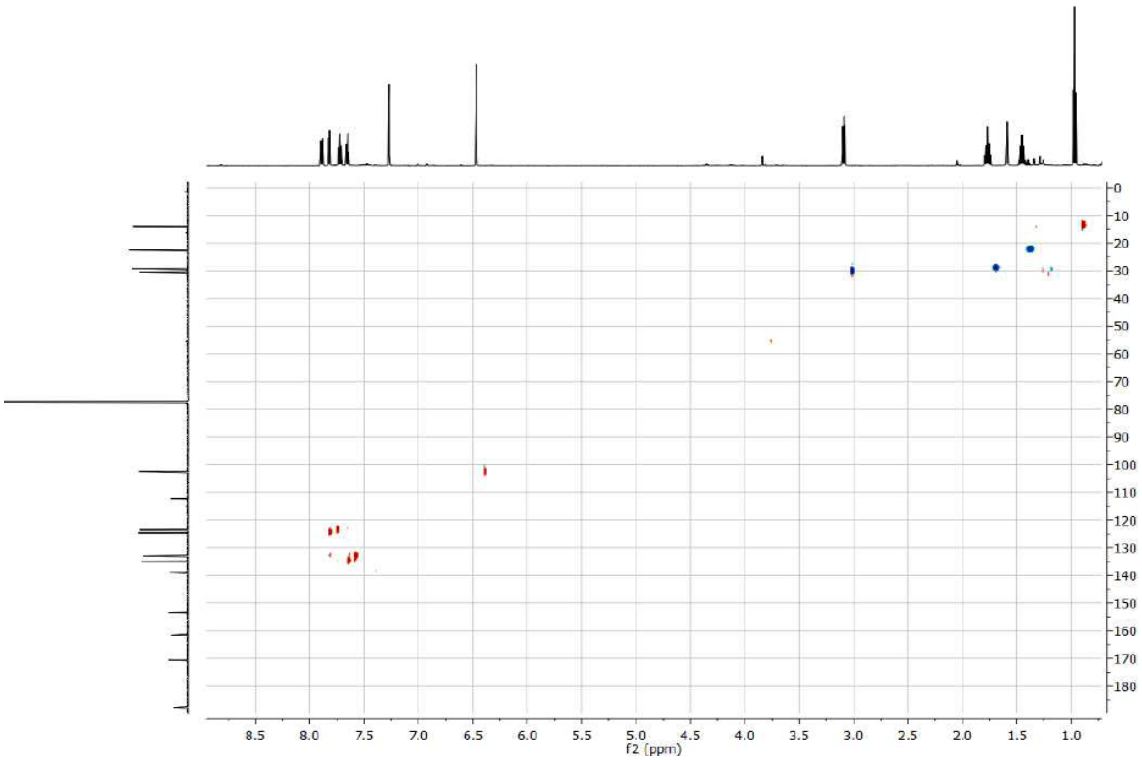
134.895
139.005
139.048
153.481
161.497
170.521
187.740

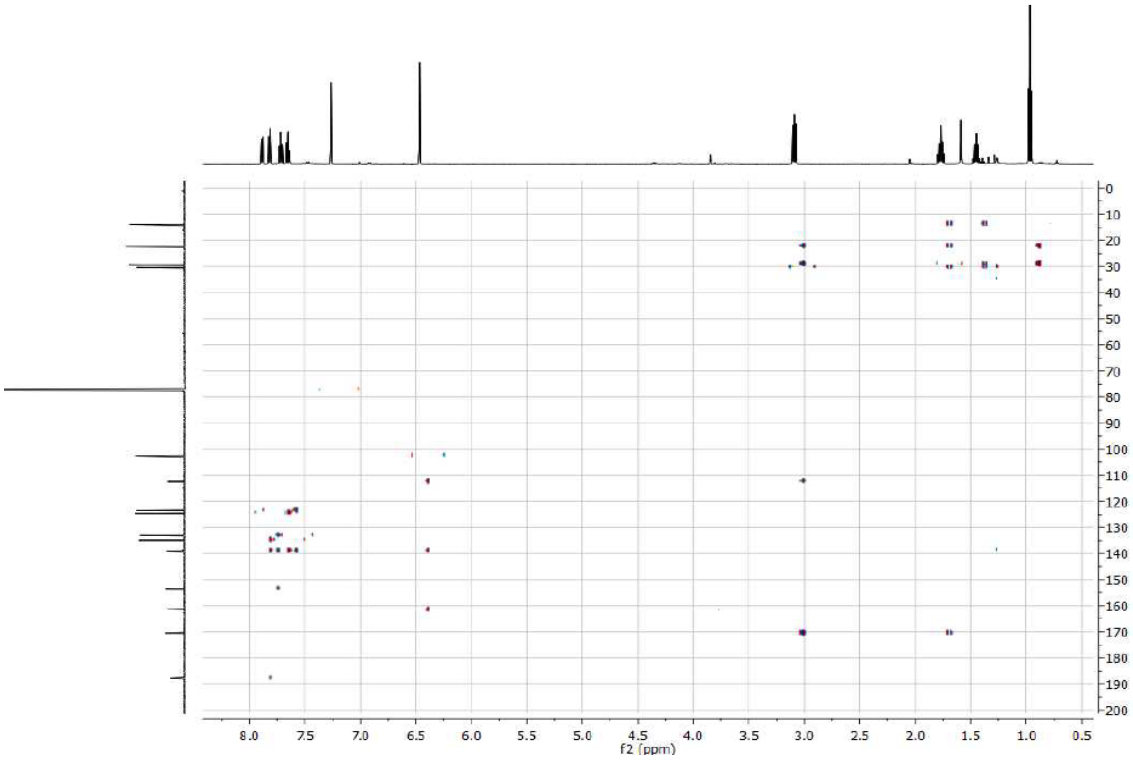
^{1}H COSY (400 MHz)

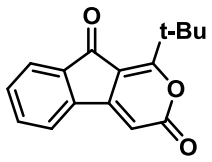


^{1}H-^{13}C HSQC (600 MHz)



^{1}H-^{13}C HMBC (600 MHz)




O
t-Bu
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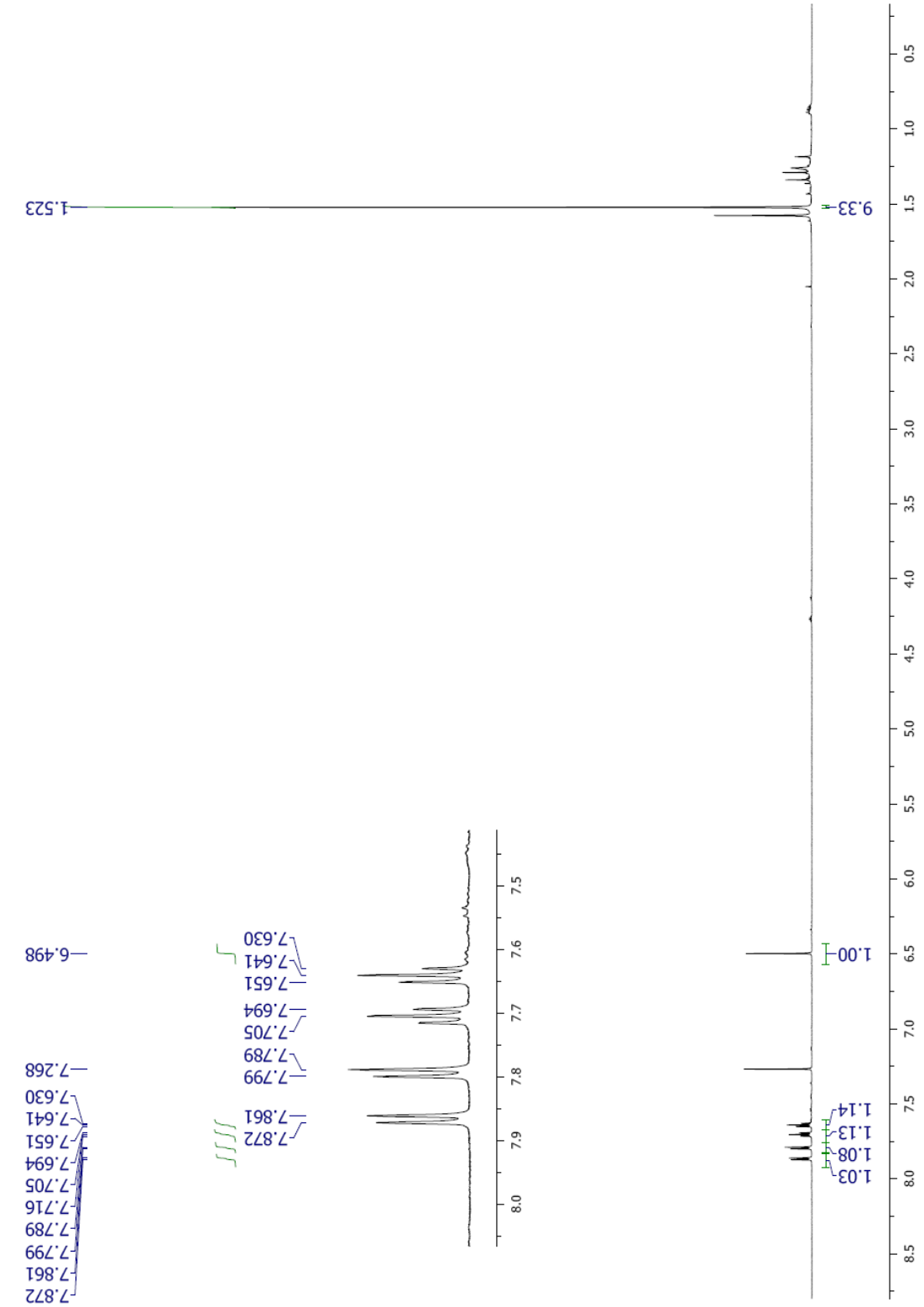
O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7.630
7.872
7.861
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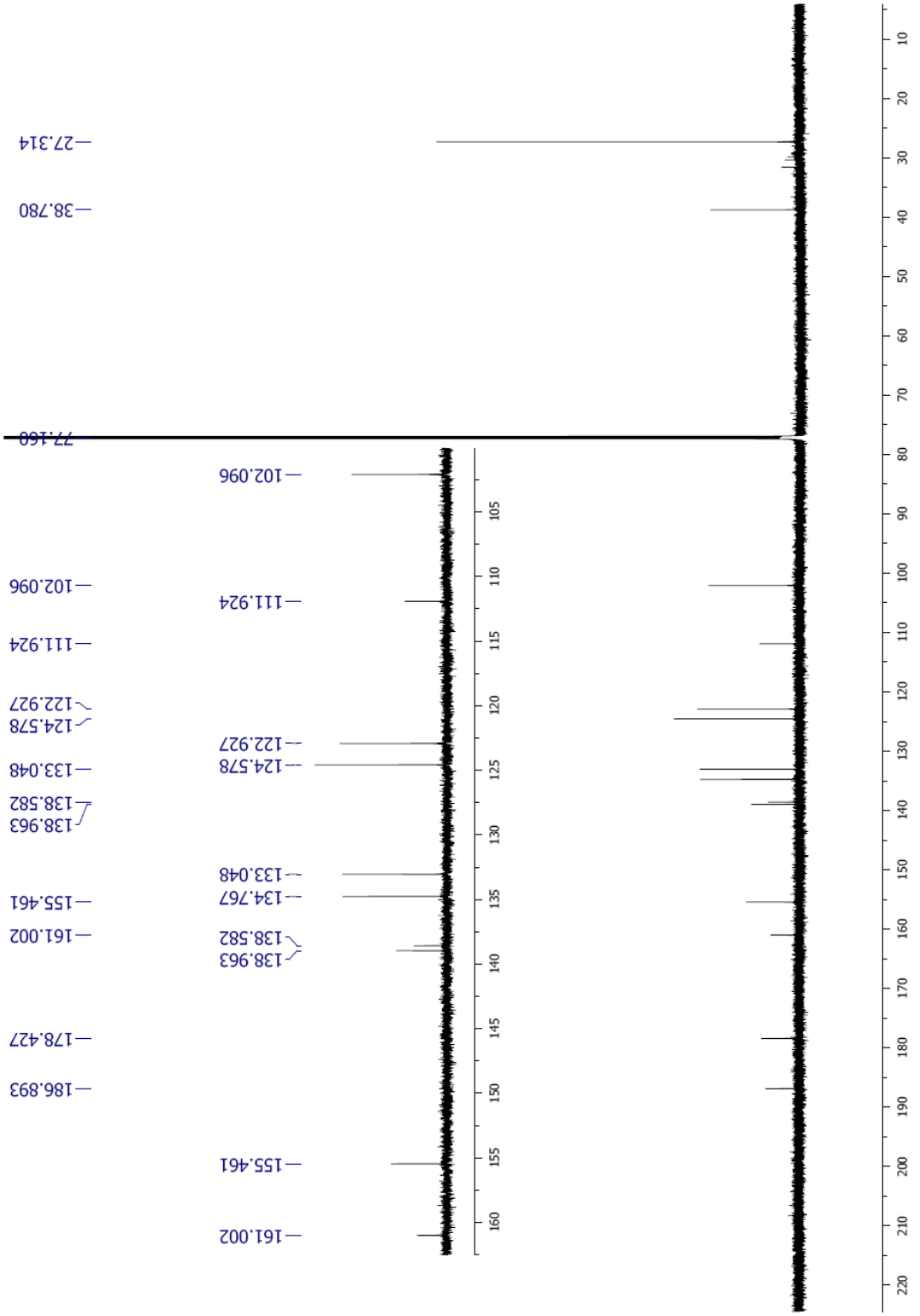
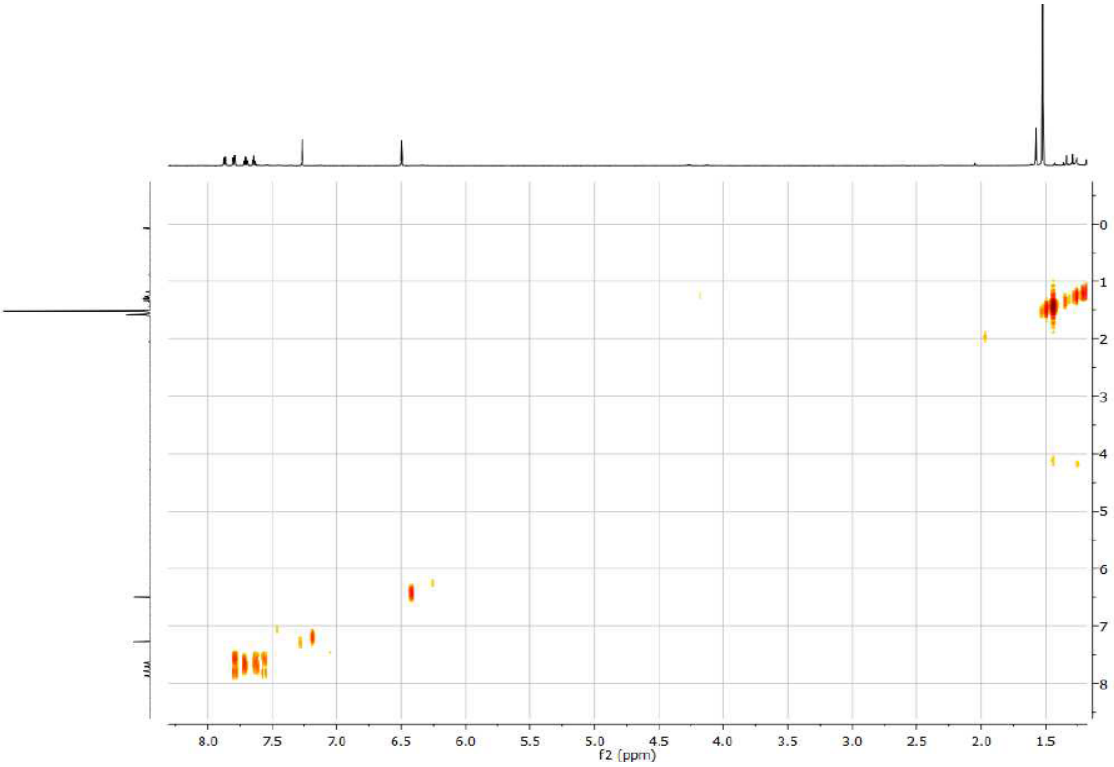
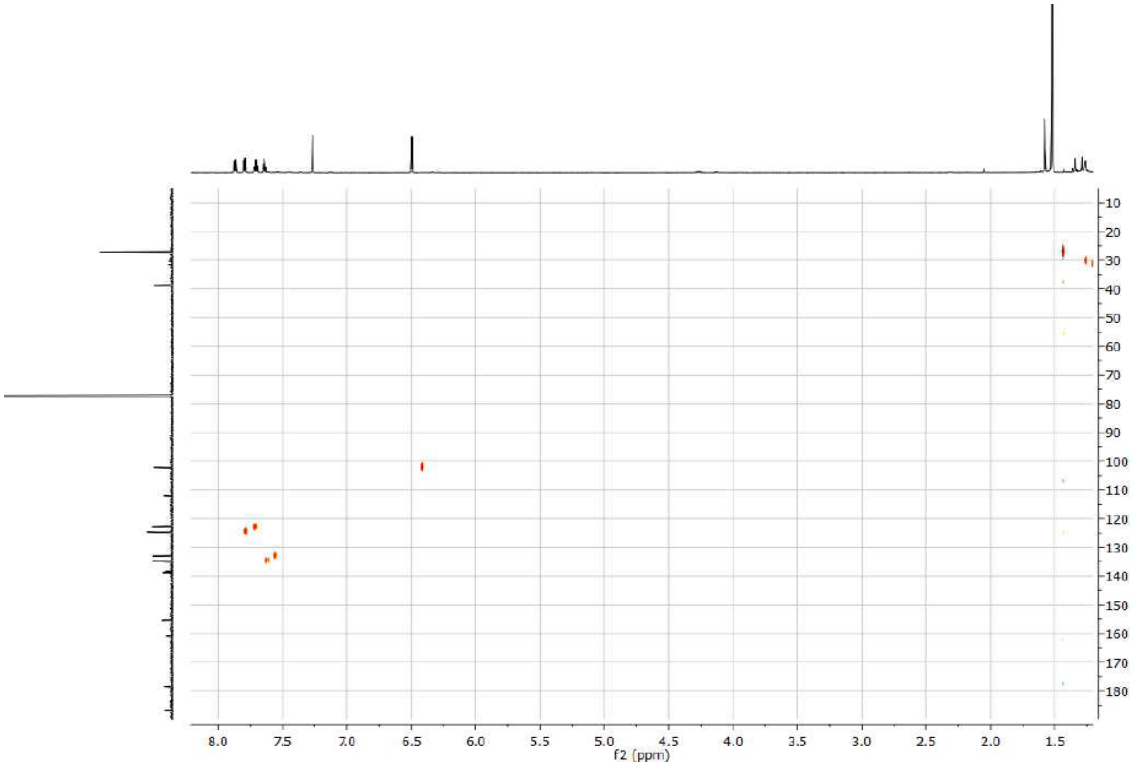
7.641
7.630
1.00
1.14
1.13
1.08
1.03



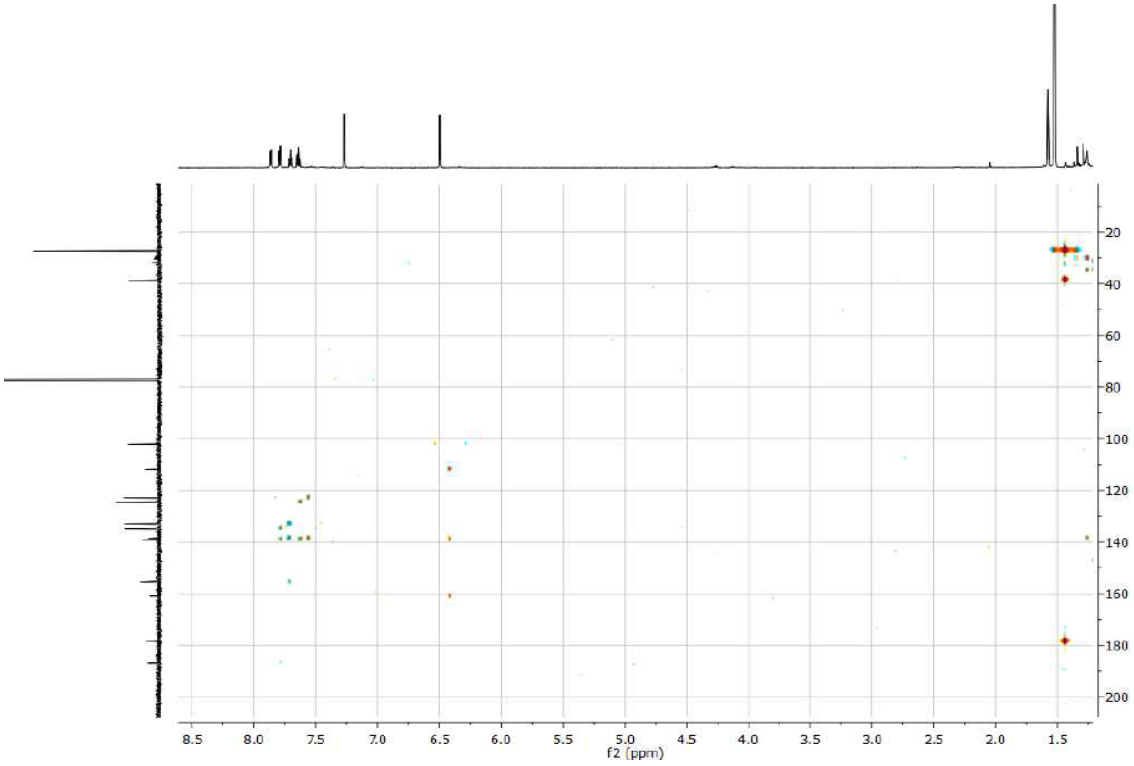
^{1}H COSY (700 MHz)

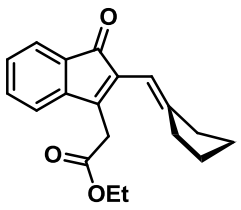


^{1}H-^{13}C HSQC (700 MHz)



^{1}H-^{13}C HMBC (700 MHz)

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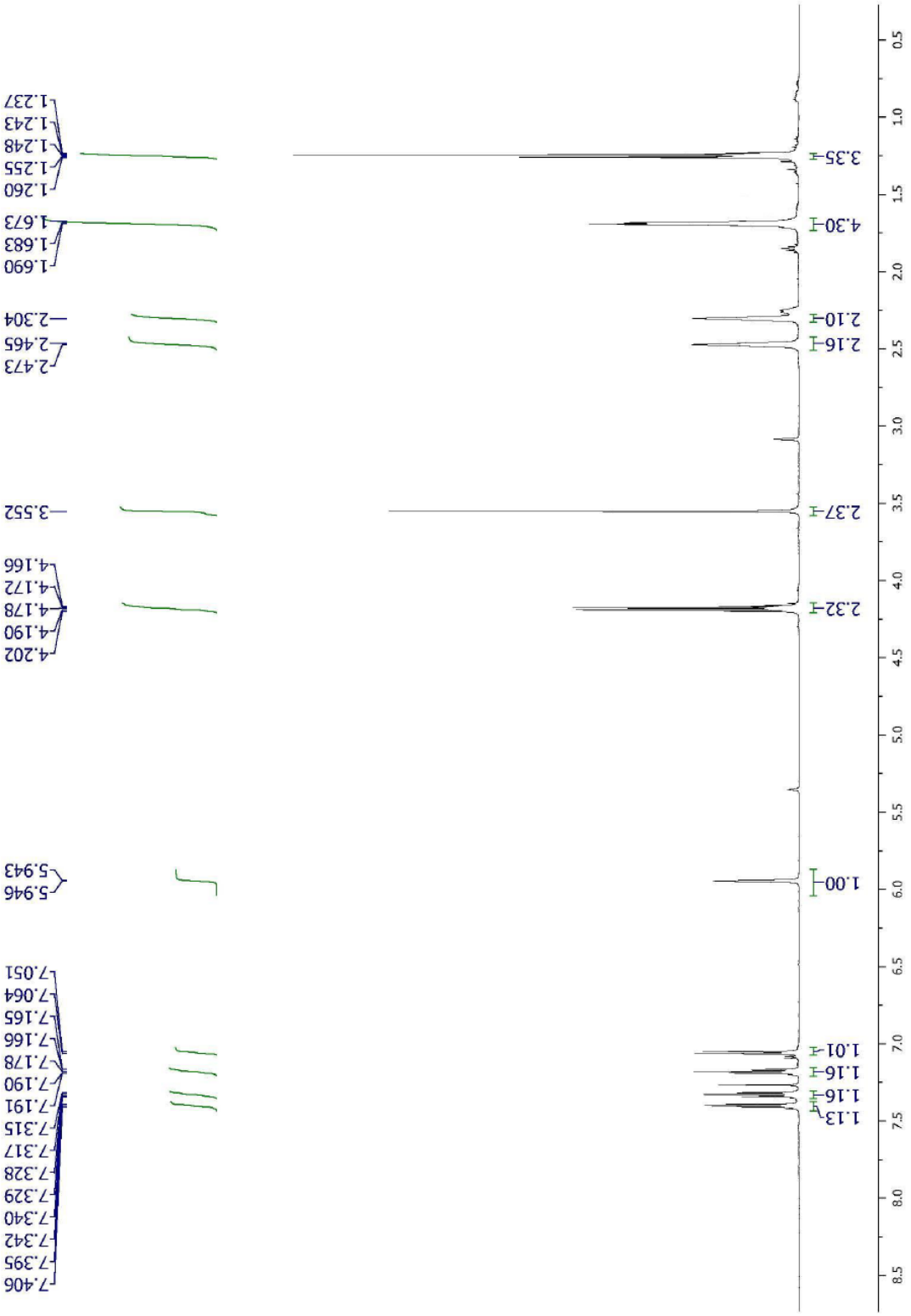
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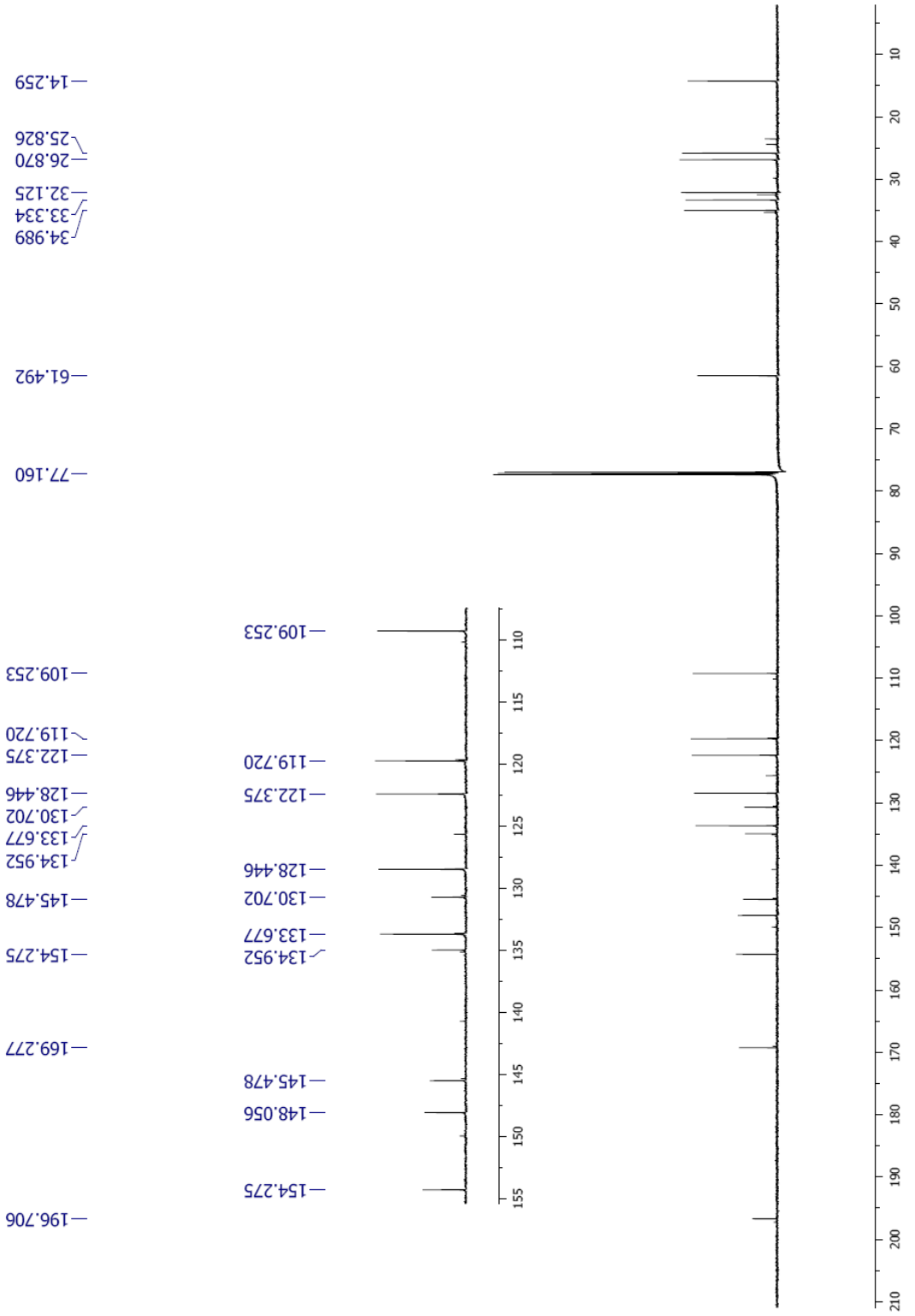
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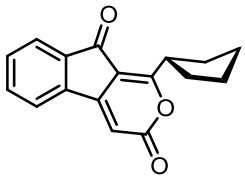
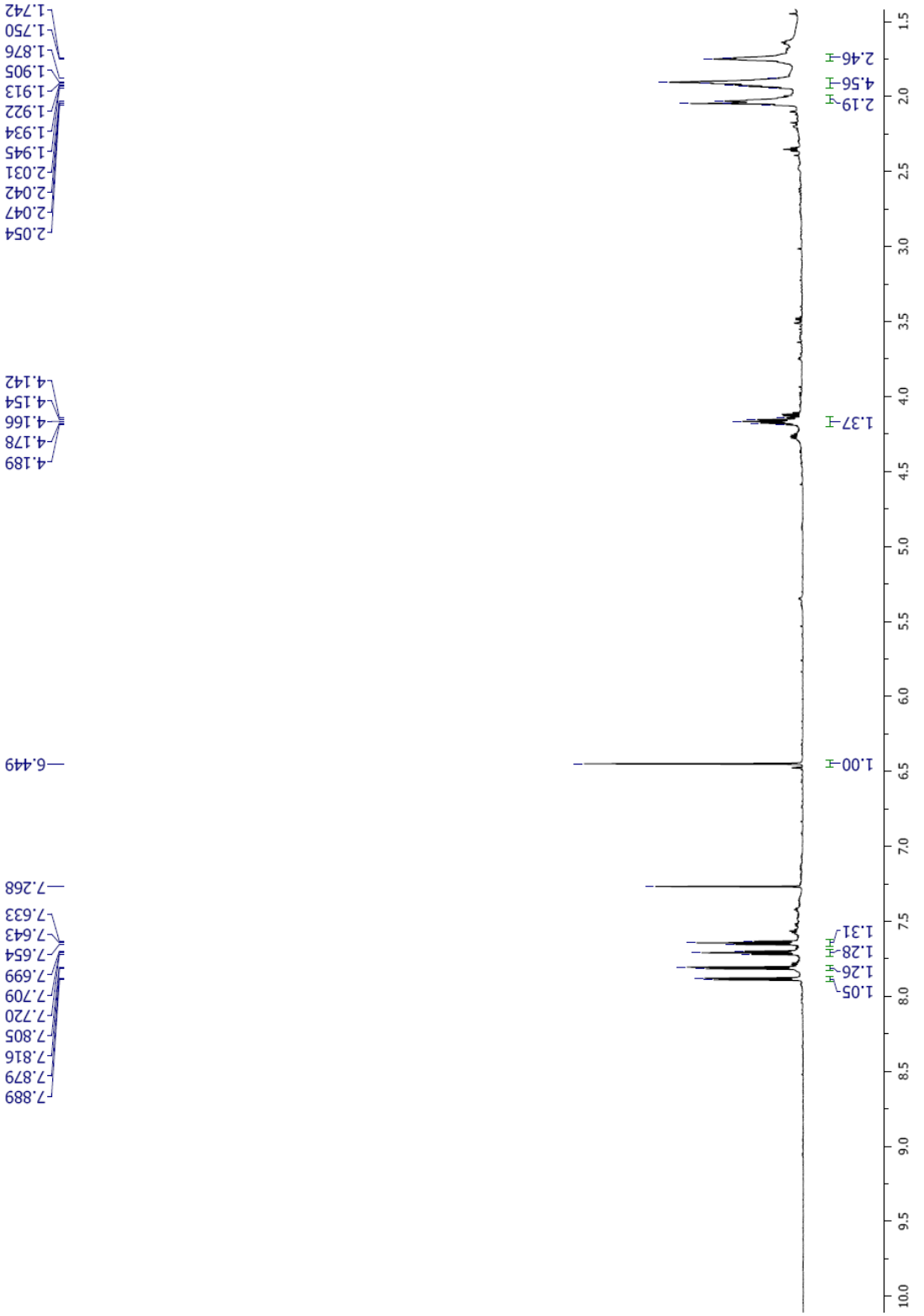
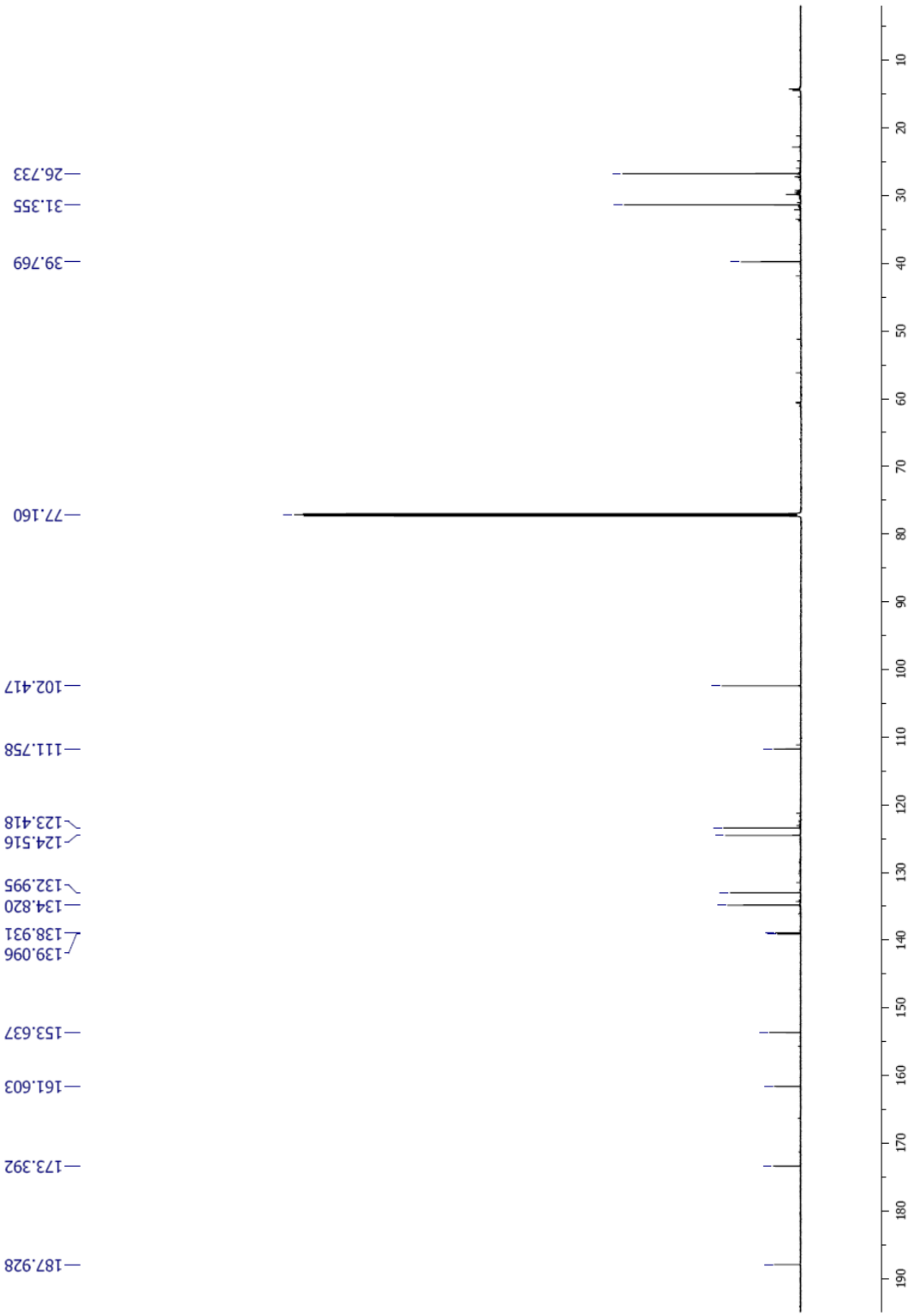
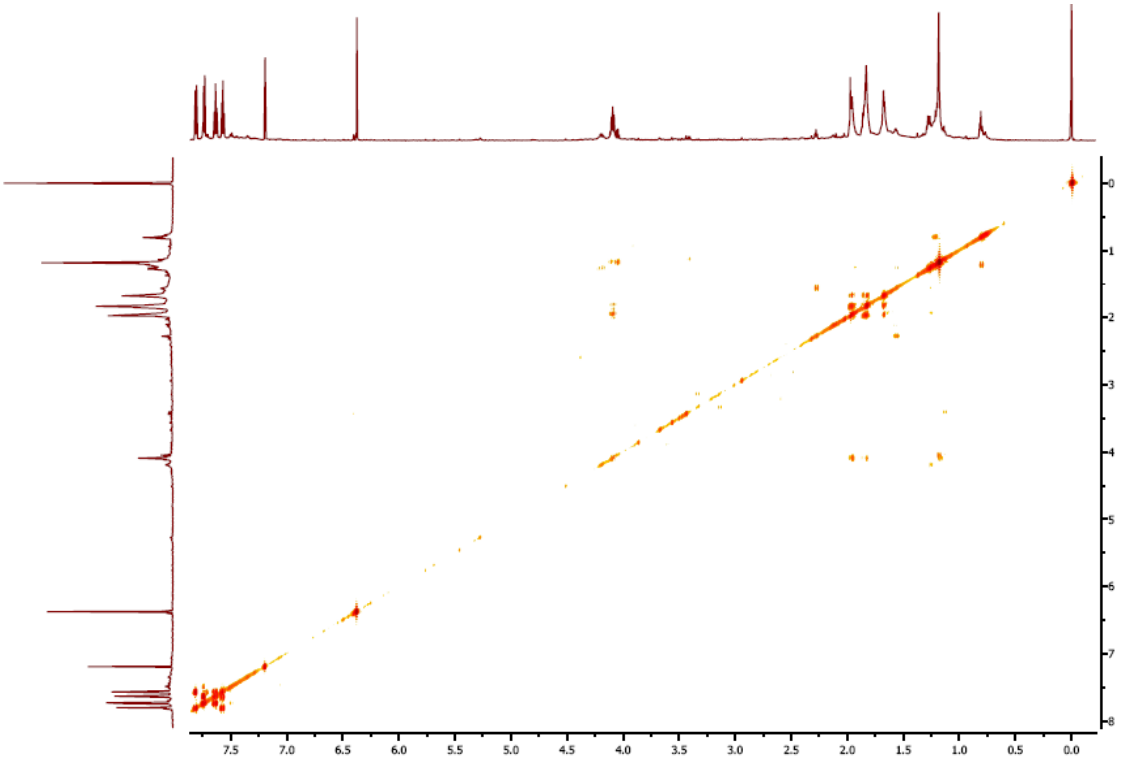
34.989
61.492
77.160
109.253
119.720
122.375
128.446
130.702
133.677
134.952
145.478
154.275
169.277
196.706



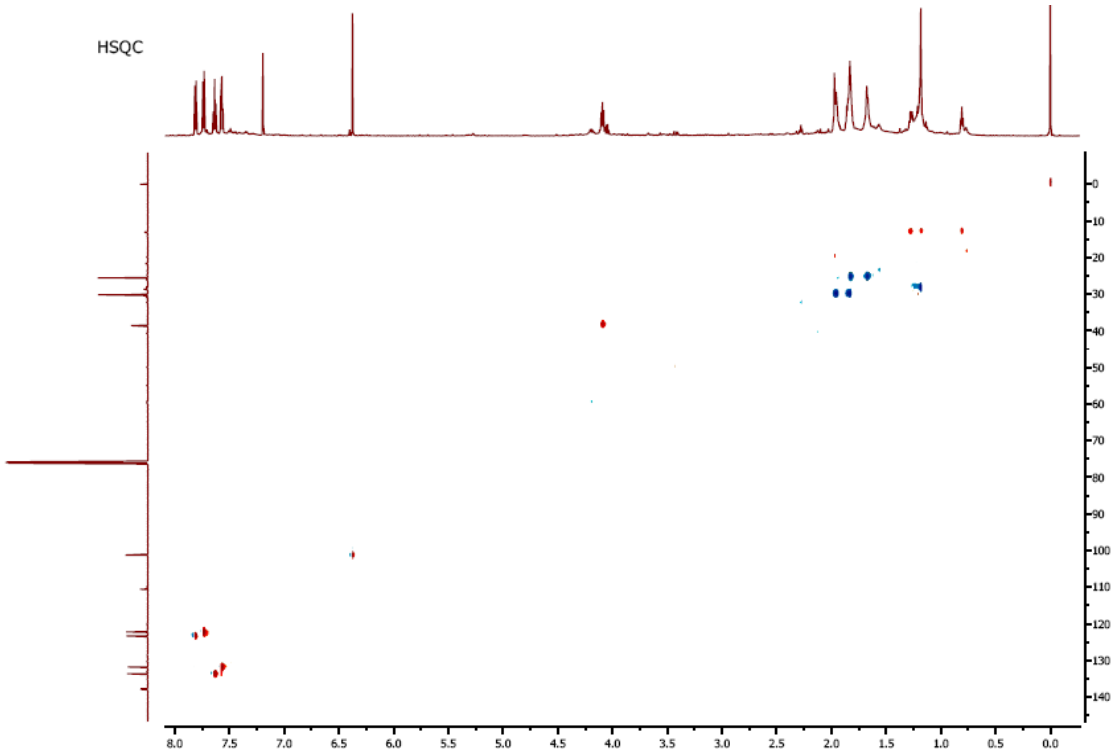

1.742
1.750
1.876
1.905
1.913
1.922
1.934
1.945
2.031
2.042
2.047
2.054
4.142
4.154
4.166
4.178
4.189
6.449
7.268
7.633
7.643
7.654
7.699
7.709
7.720
7.805
7.816
7.879
7.889
2.46
4.56
2.19
1.37
1.00
1.31
1.28
1.26
1.05
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0


26.733
31.355
39.769
77.160
102.417
111.758
123.418
124.516
132.995
134.820
138.931
139.096
153.637
161.603
173.392
187.928
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190

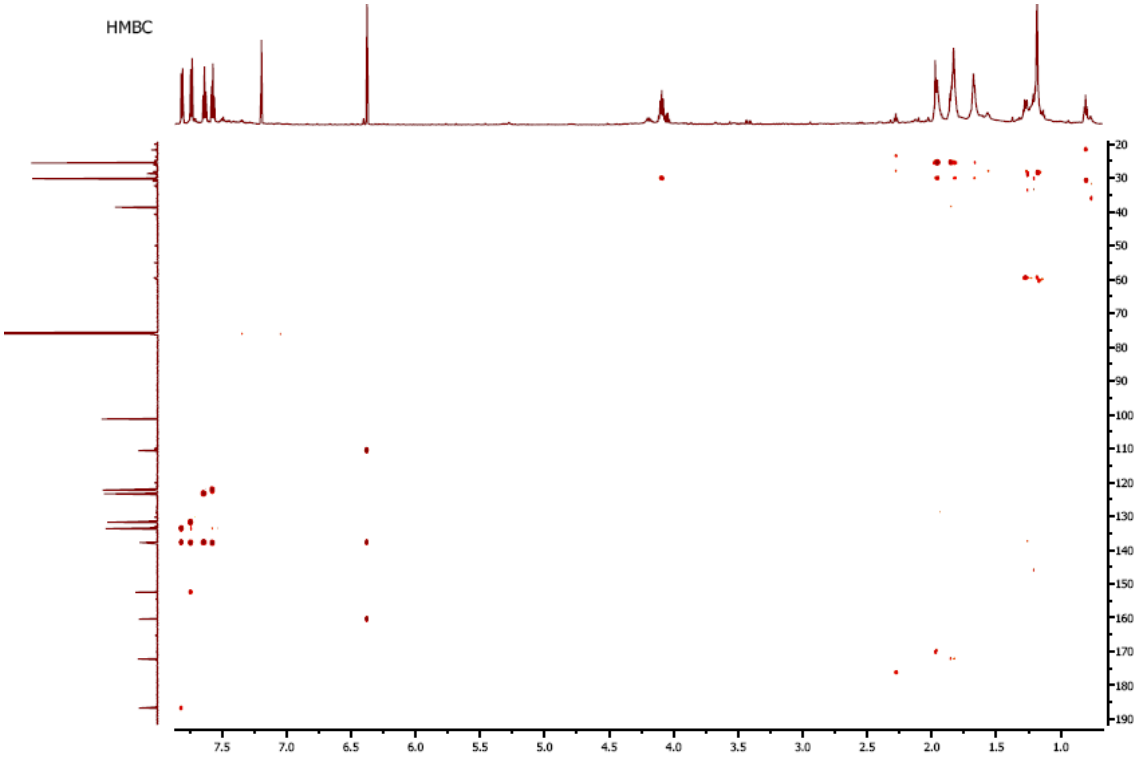
^{1}H COSY (700 MHz)

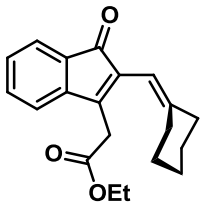


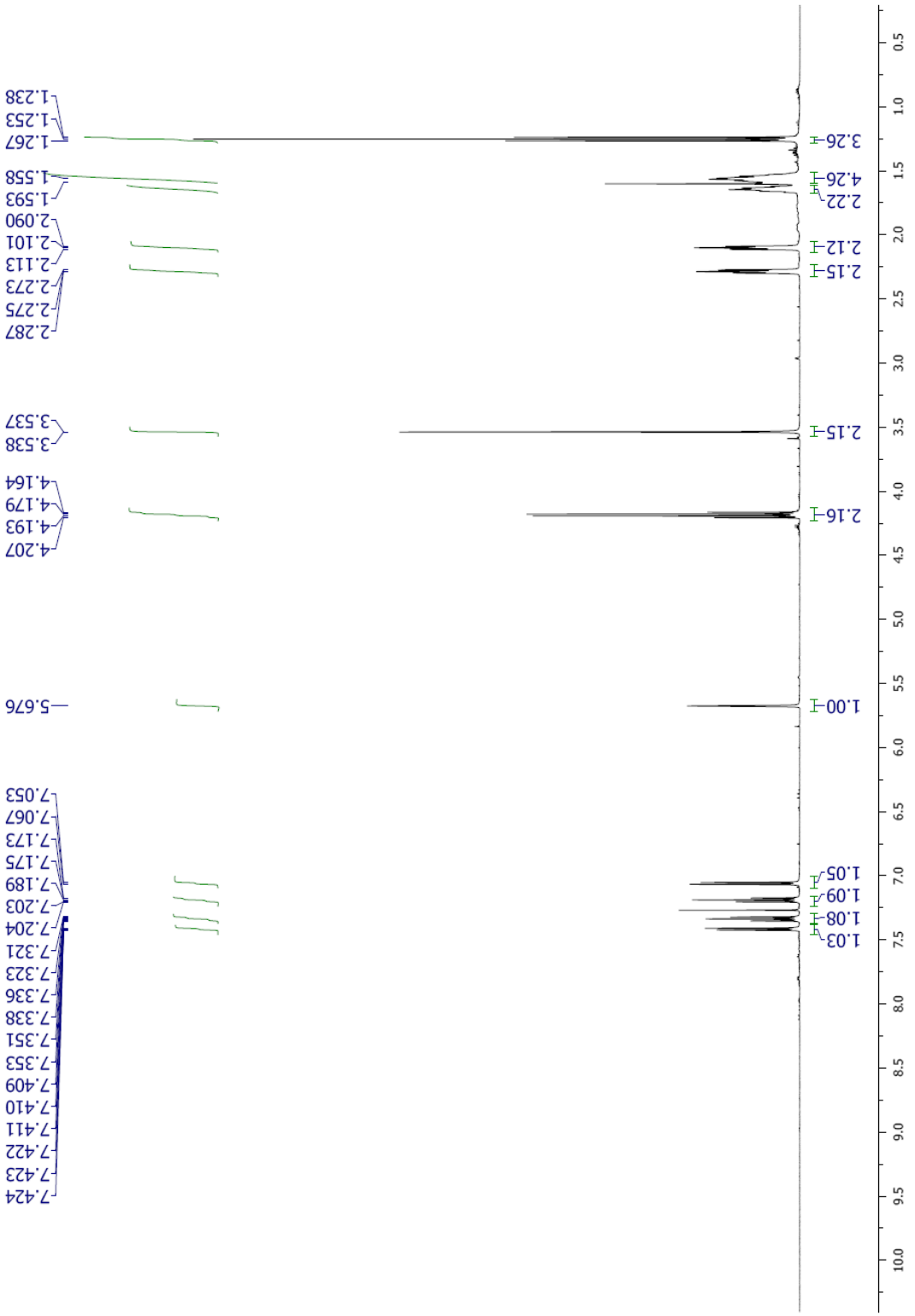
^{1}H-^{13}C HSQC (700 MHz)

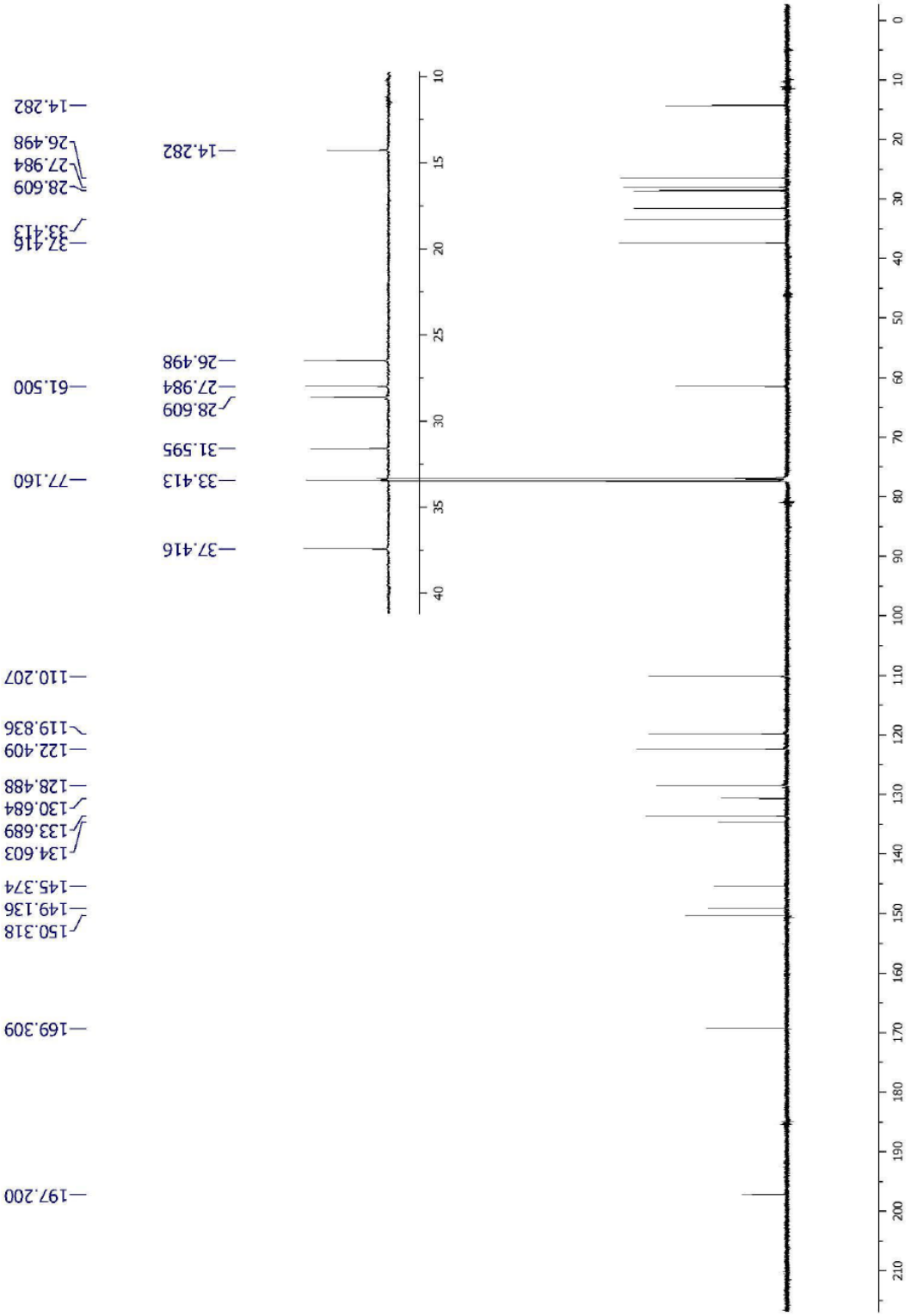


^{1}H-^{13}C HMBC (700 MHz)

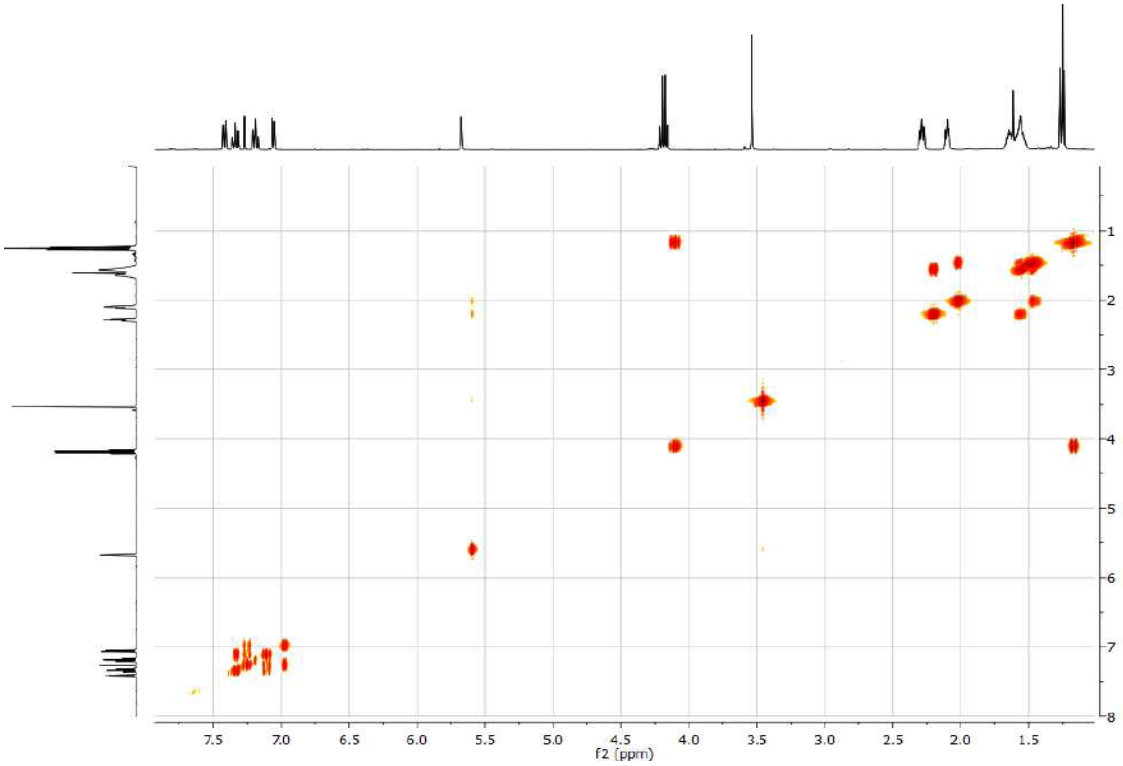



O
O
OEt

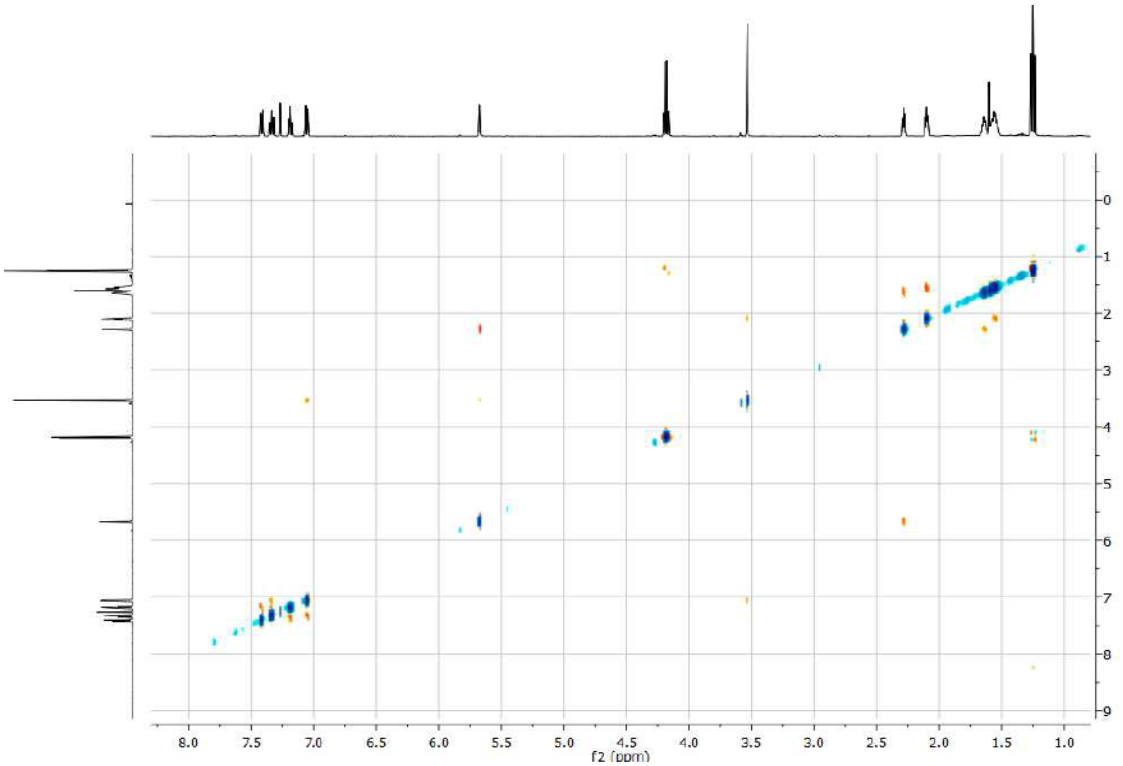

1.238
1.253
1.267
1.558
1.593
2.090
2.101
2.113
2.273
2.275
2.287
3.537
3.538
4.164
4.179
4.193
4.207
5.676
7.053
7.067
7.173
7.175
7.189
7.203
7.204
7.321
7.323
7.336
7.338
7.351
7.353
7.409
7.410
7.411
7.422
7.423
7.424
3.26
4.26
2.22
2.12
2.15
2.15
2.16
1.00
1.05
1.09
1.08
1.03


14.282
26.498
27.984
28.609
33.413
37.416
61.500
77.160
110.207
119.836
122.409
128.488
130.684
133.689
134.603
145.374
149.136
150.318
169.309
197.200

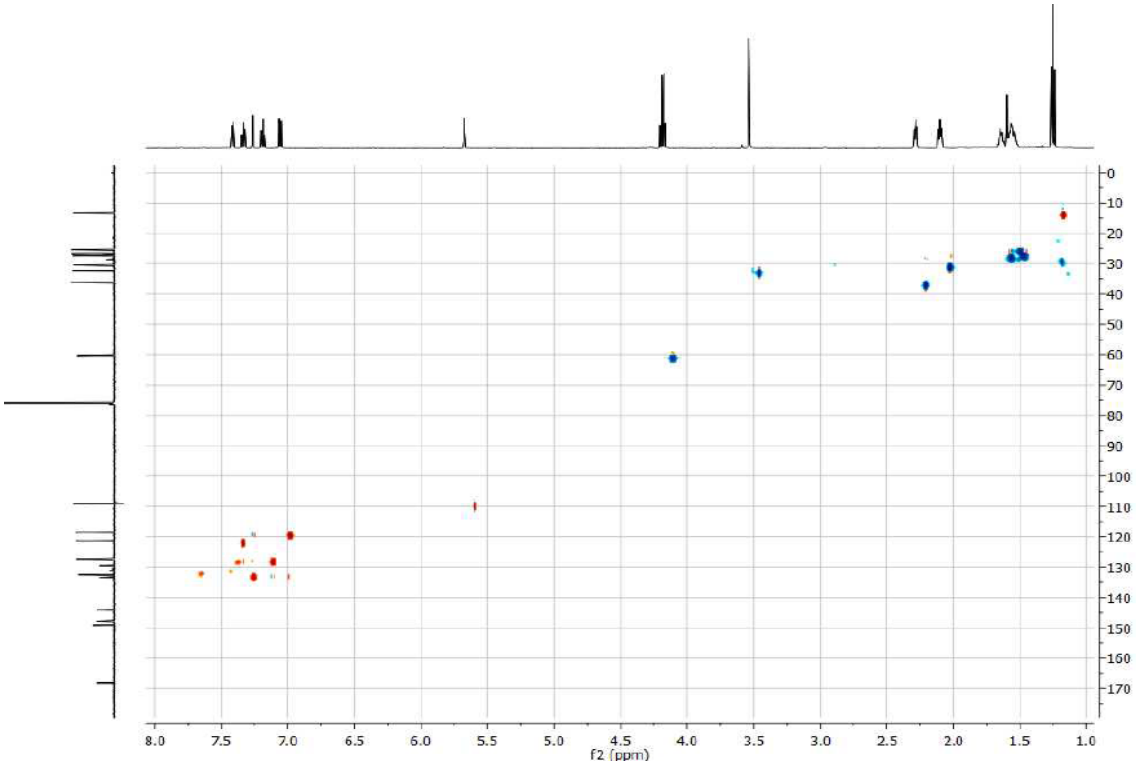
^{1}H COSY (400 MHz)



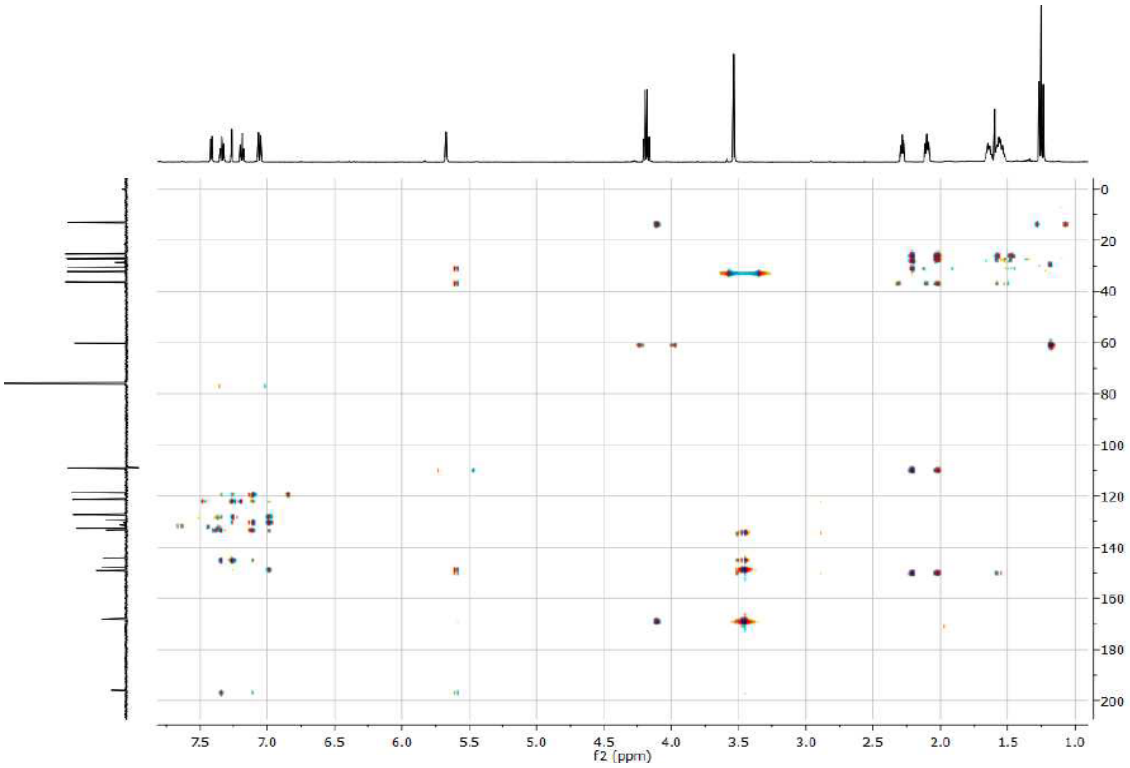
^{1}H NOESY (500 MHz)

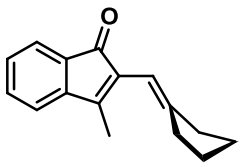


^{1}H-^{13}C HSQC (600 MHz)



^{1}H-^{13}C HMBC (600 MHz)

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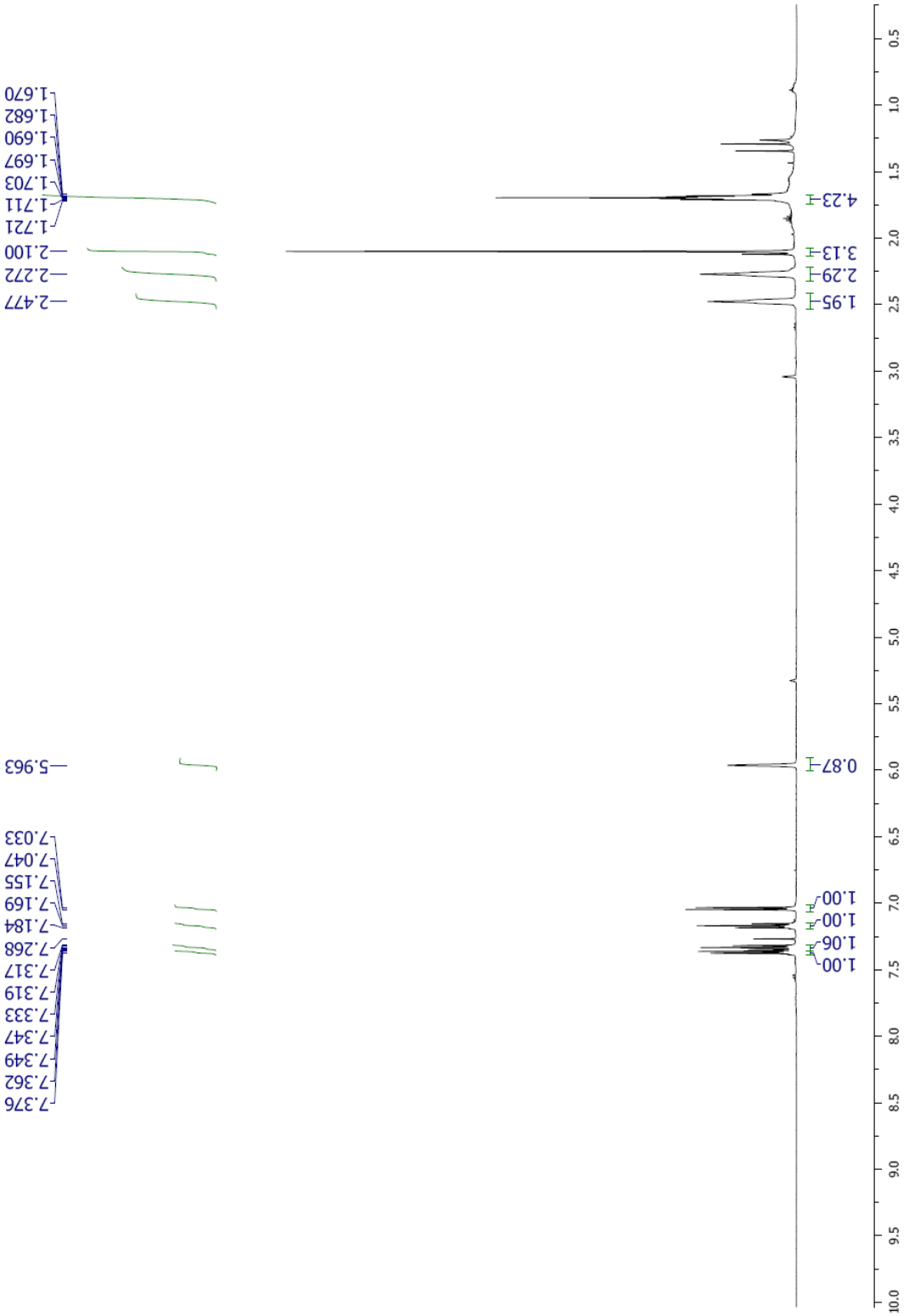
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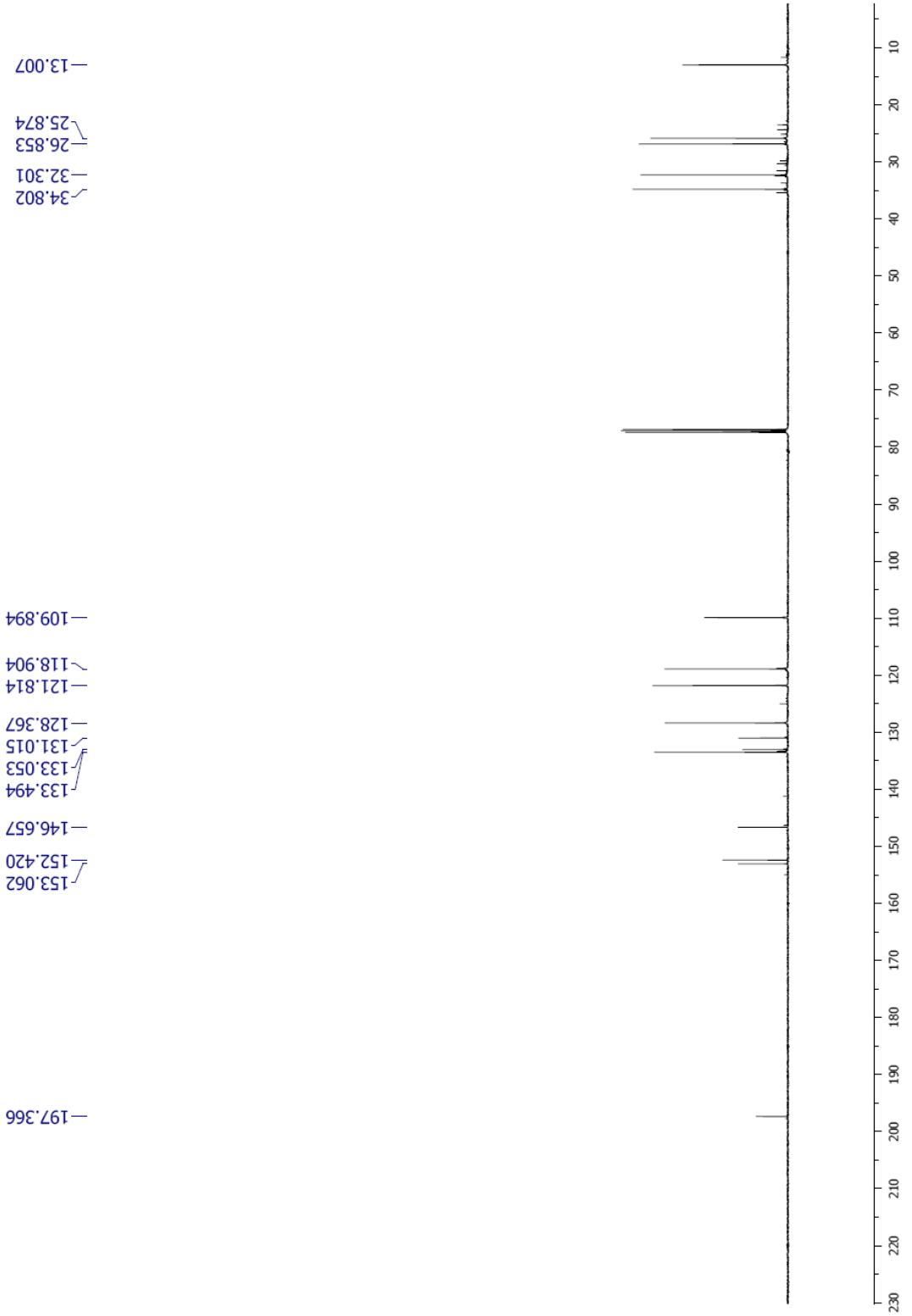
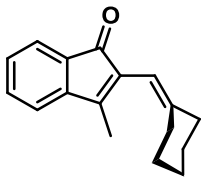
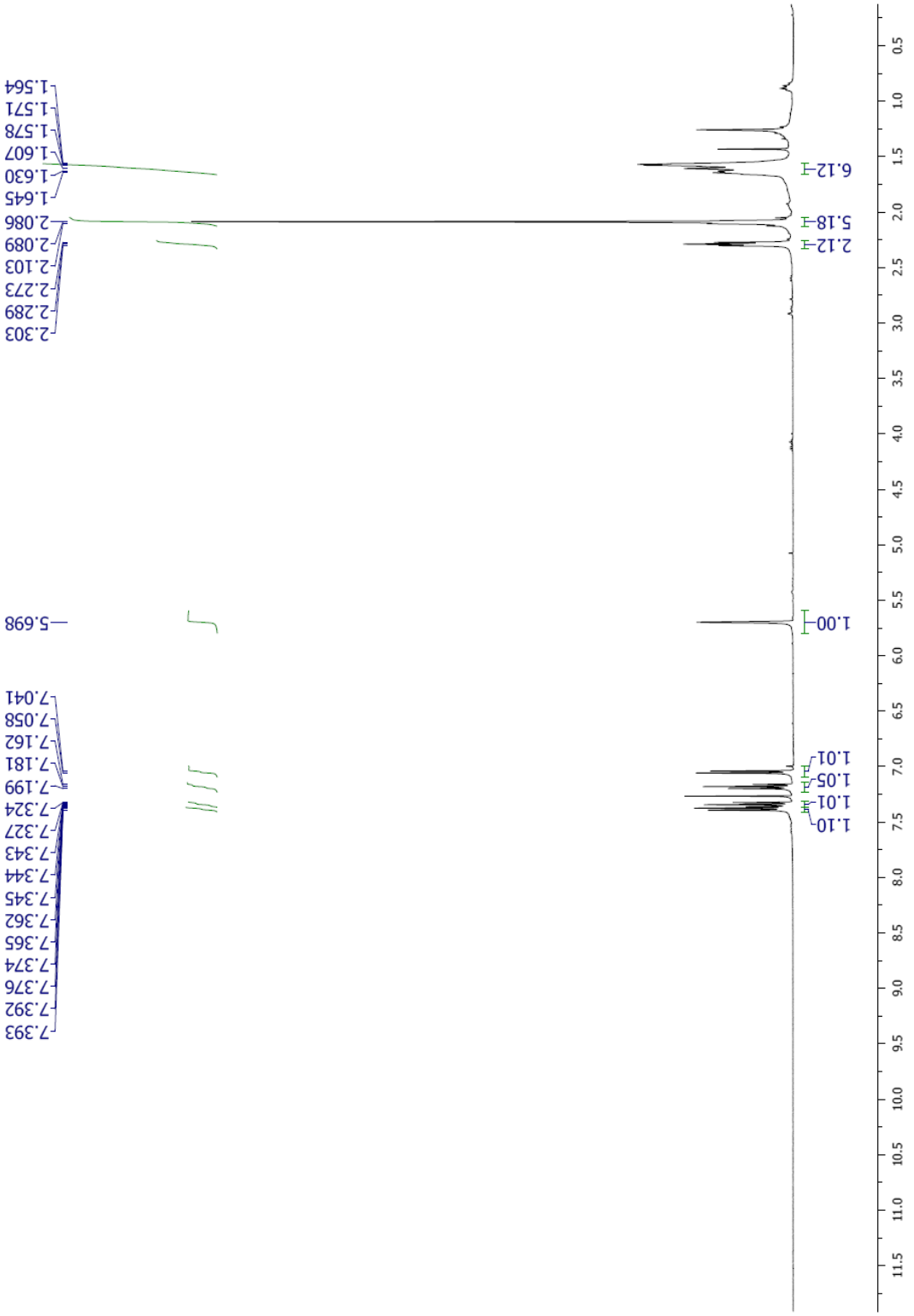
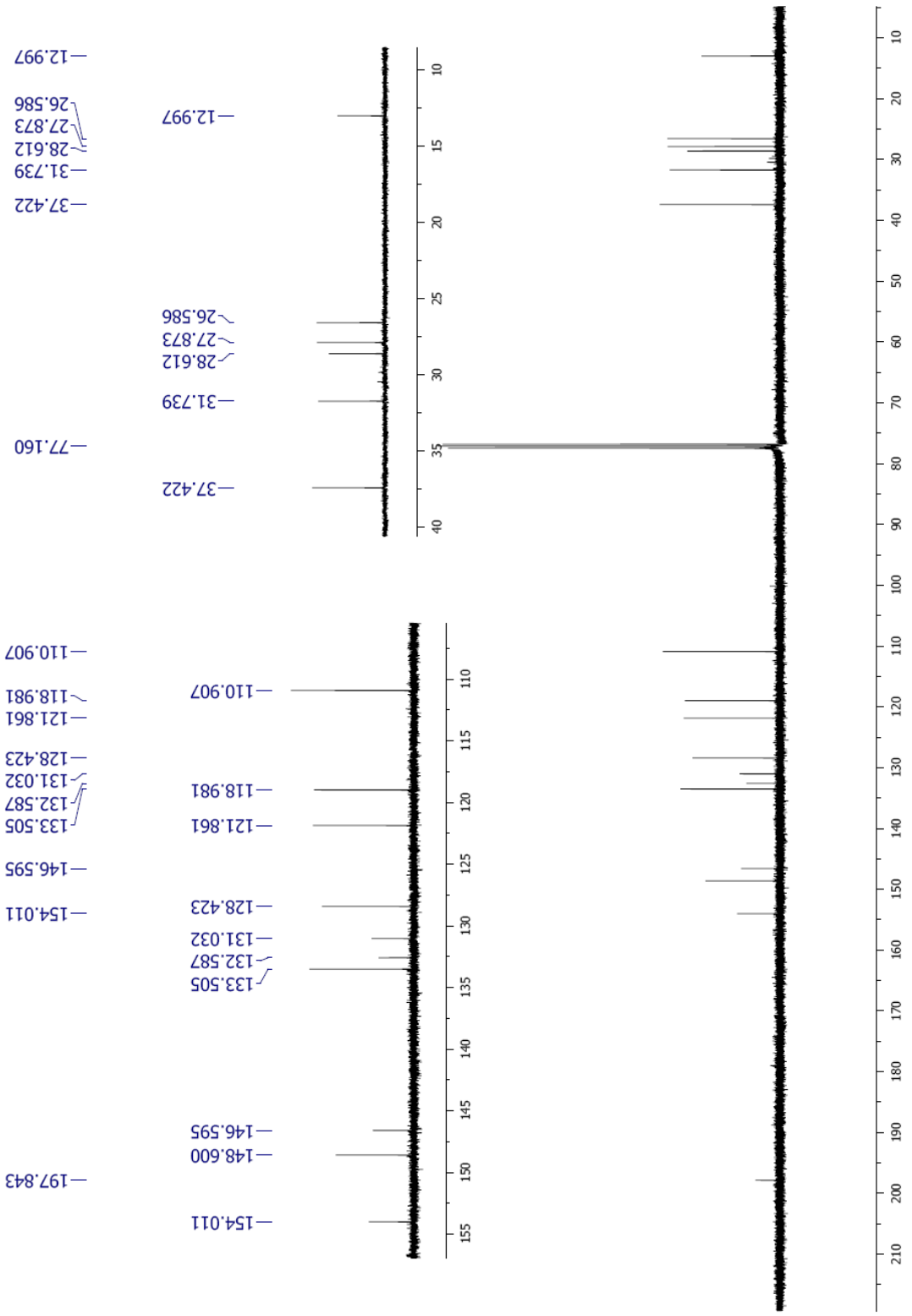
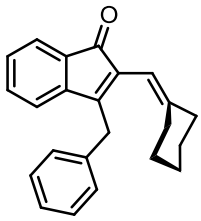
1.682
1.690
1.697
1.703
1.711
1.721
2.100
2.272
2.477
5.963
7.033
7.047
7.155
7.169
7.184
7.268
7.317
7.319
7.333
7.347
7.349
7.362
7.376
4.23
3.13
2.29
1.95
0.87
1.00
1.00
1.06
1.00

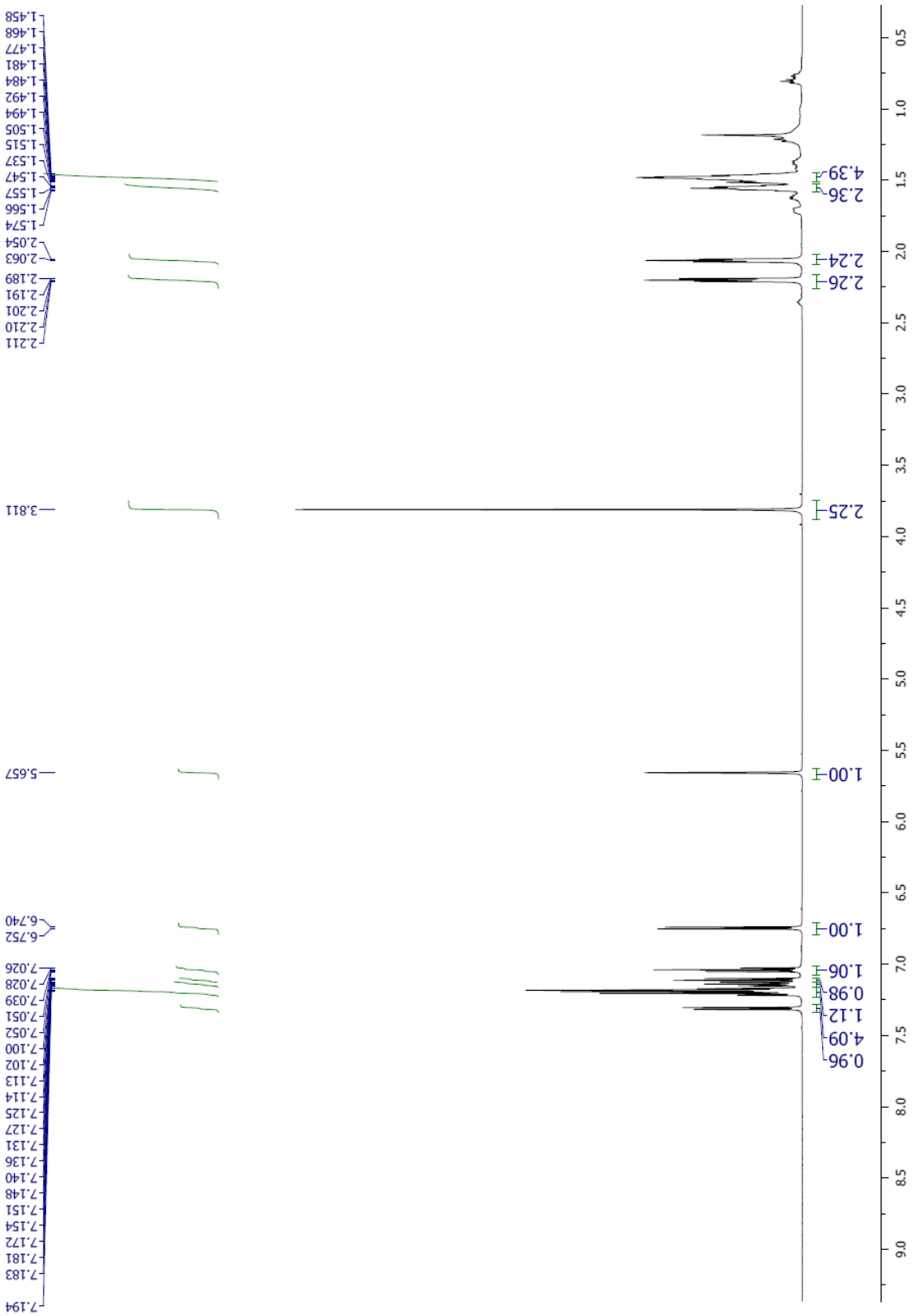

13.007
25.874
26.853
32.301
34.802
109.894
118.904
121.814
128.367
131.015
133.053
133.494
146.657
152.420
153.062
197.366
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
220
230




1.564
1.571
1.578
1.607
1.630
1.645
2.086
2.089
2.103
2.273
2.289
2.303
5.698
7.041
7.058
7.162
7.181
7.199
7.324
7.327
7.343
7.344
7.345
7.362
7.365
7.374
7.376
7.392
7.393
6.12
5.18
2.12
1.00
1.01
1.05
1.01
1.10


12.997
26.586
27.873
28.612
31.739
37.422
77.160
110.907
118.981
121.861
128.423
131.032
132.587
133.505
146.595
154.011
197.843

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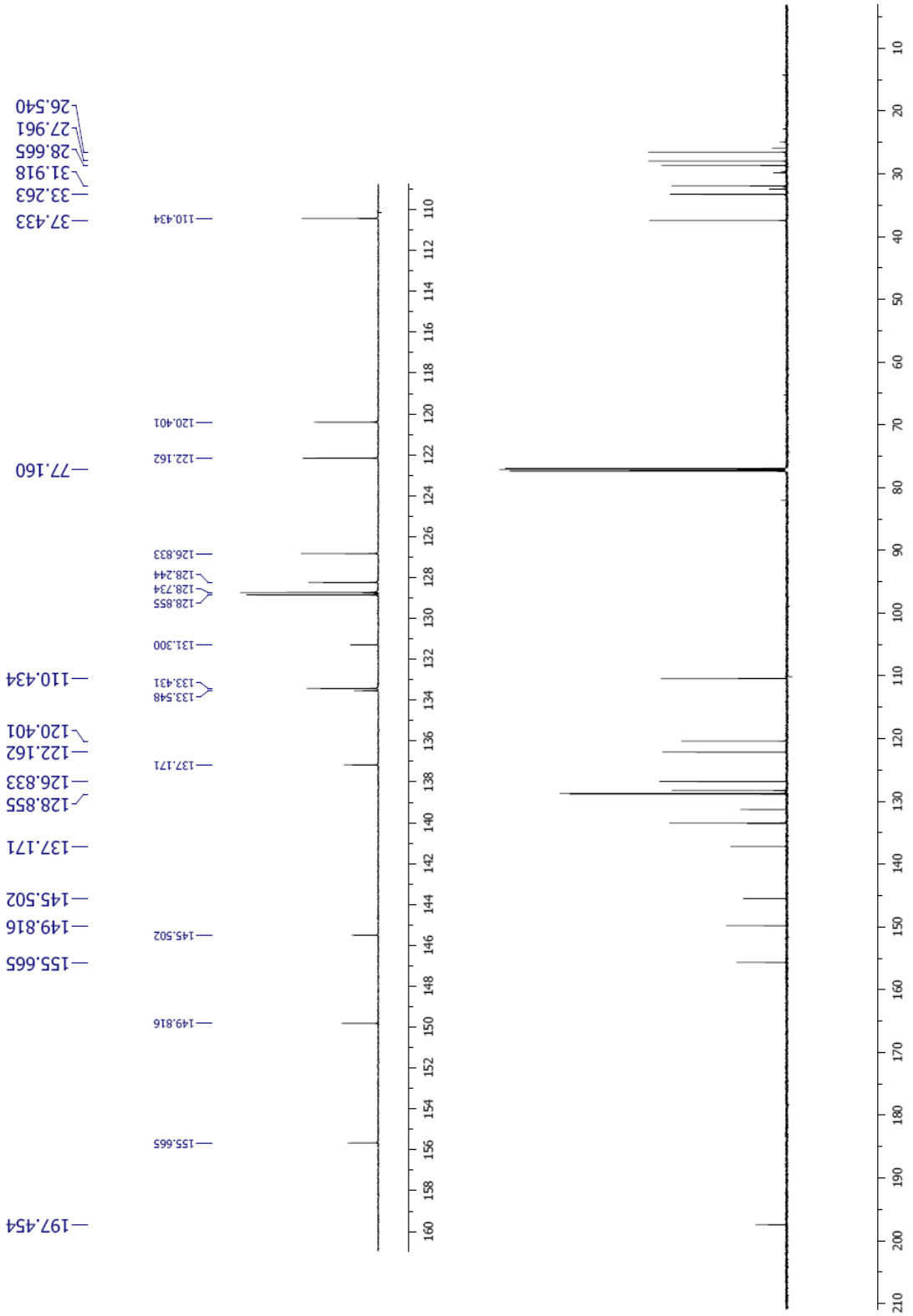
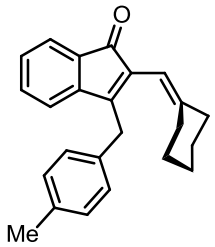
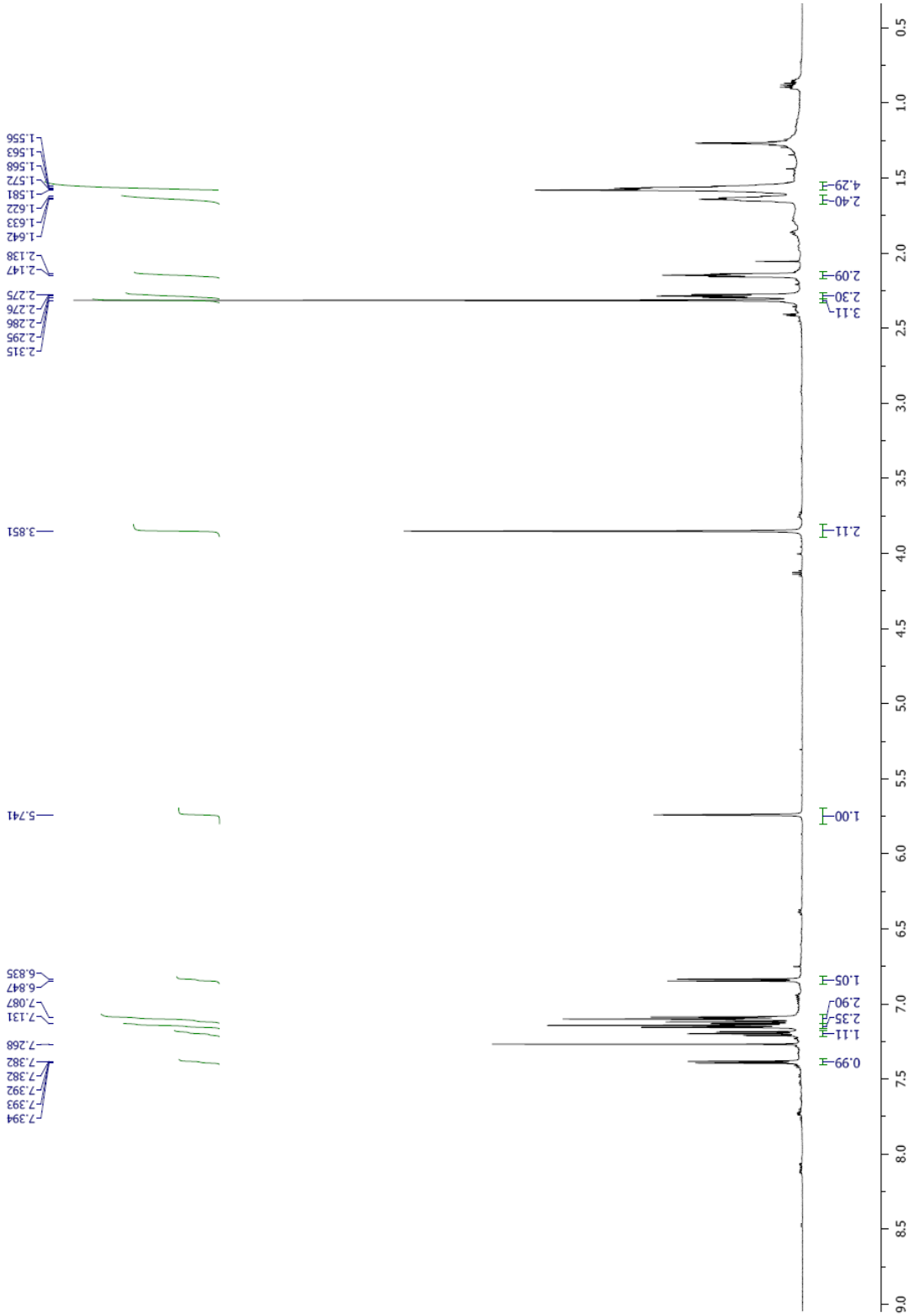
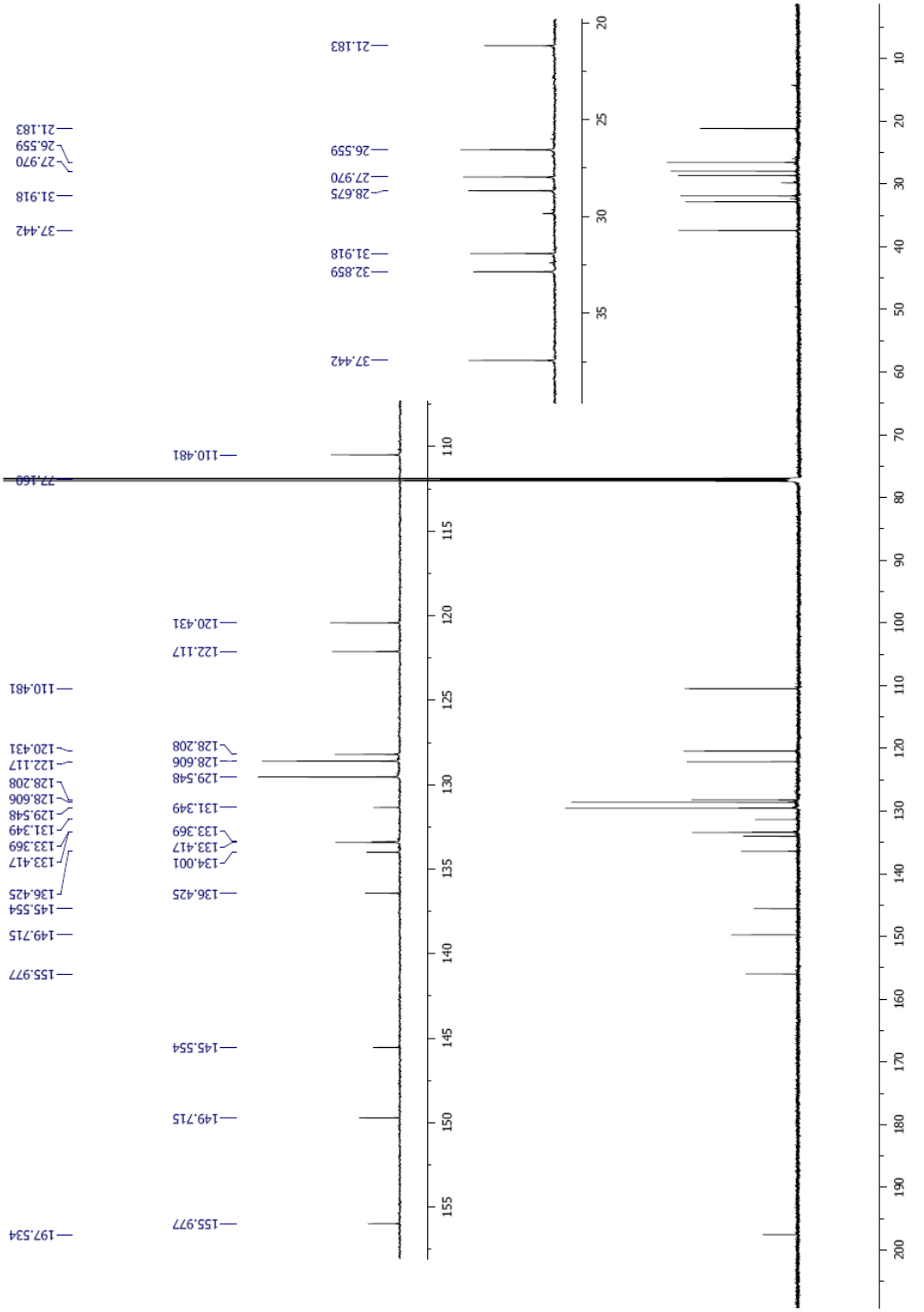
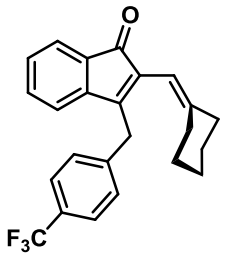
1.468
1.477
1.481
1.484
1.492
1.494
1.505
1.515
1.537
1.547
1.557
1.566
1.574
2.054
2.063
2.189
2.191
2.201
2.210
2.211
3.811
5.657
6.740
6.752
7.026
7.028
7.039
7.051
7.052
7.100
7.102
7.113
7.114
7.125
7.127
7.131
7.136
7.140
7.148
7.151
7.154
7.172
7.181
7.183
7.194
4.39
2.36
2.24
2.26
2.25
1.00
1.00
1.06
0.98
1.12
4.09
0.96
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0

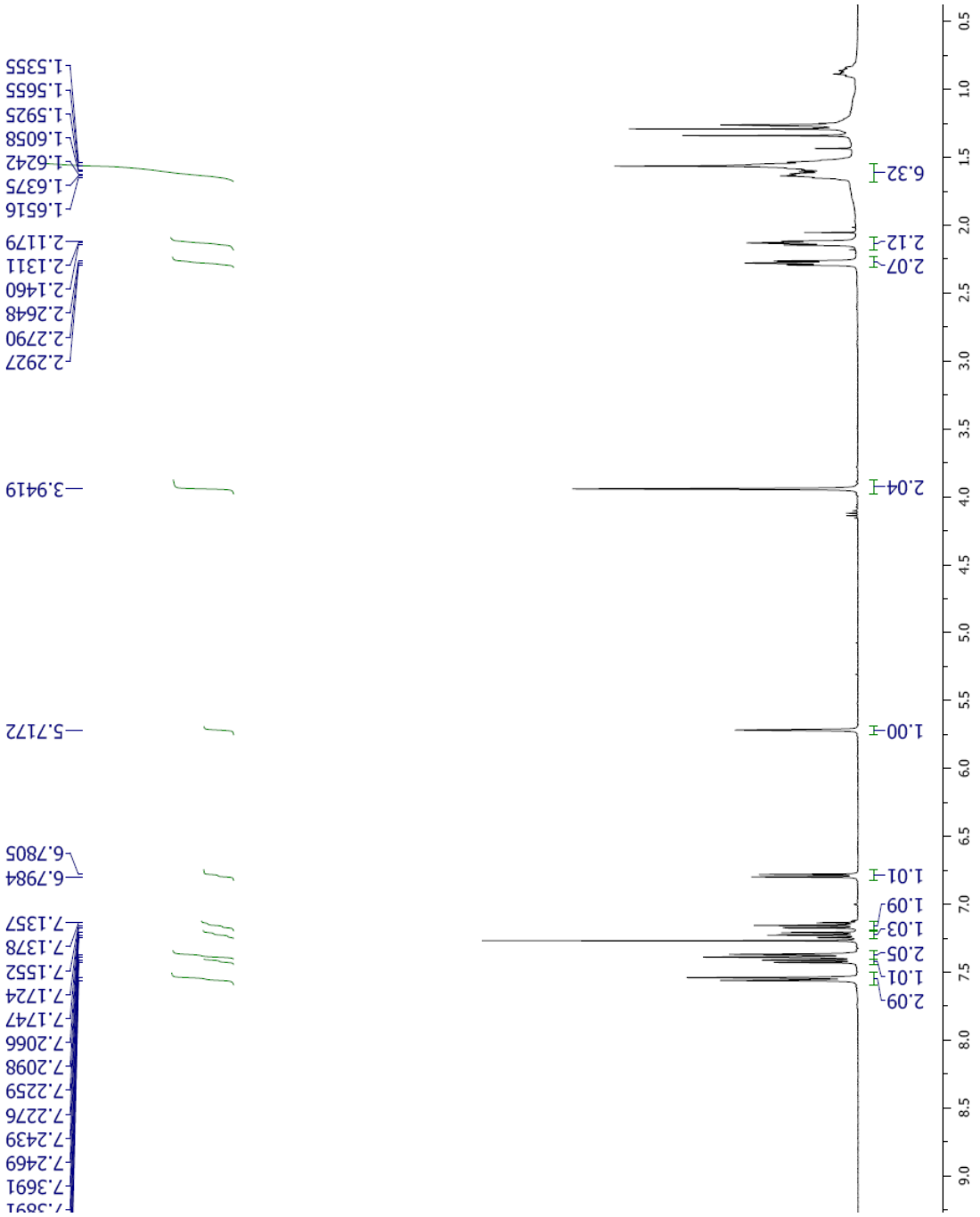

26.540
27.961
28.665
31.918
33.263
37.433
77.160
110.434
120.401
122.162
126.833
128.855
137.171
145.502
149.816
155.665
197.454

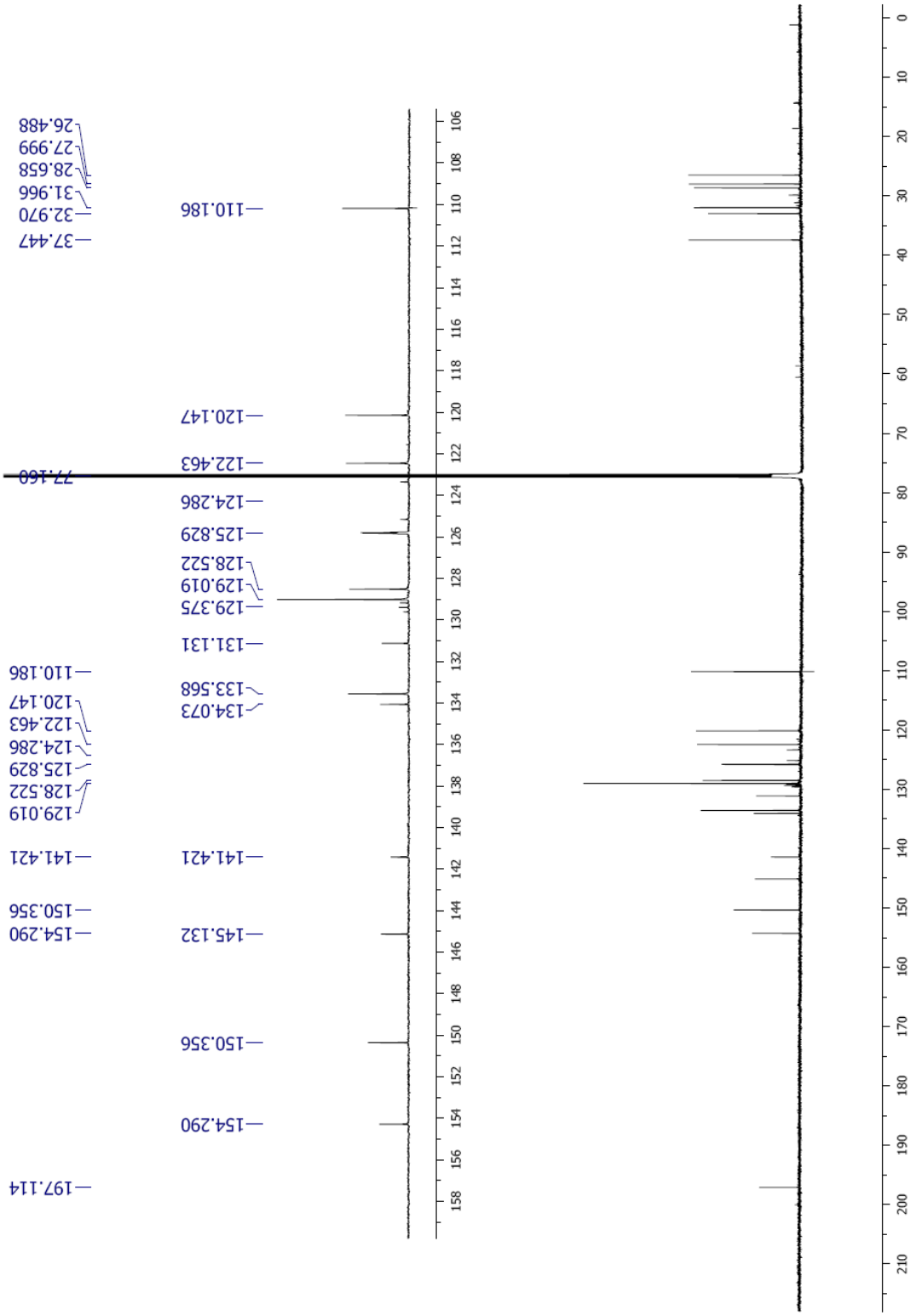

O
Me


1.556
1.563
1.568
1.572
1.581
1.622
1.633
1.642
2.138
2.147
2.275
2.276
2.286
2.295
2.315
3.851
5.741
6.835
6.847
7.087
7.131
7.268
7.382
7.382
7.392
7.393
7.394
4.29
2.40
2.09
2.30
3.11
2.11
1.00
1.05
2.90
2.35
1.11
0.99
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0

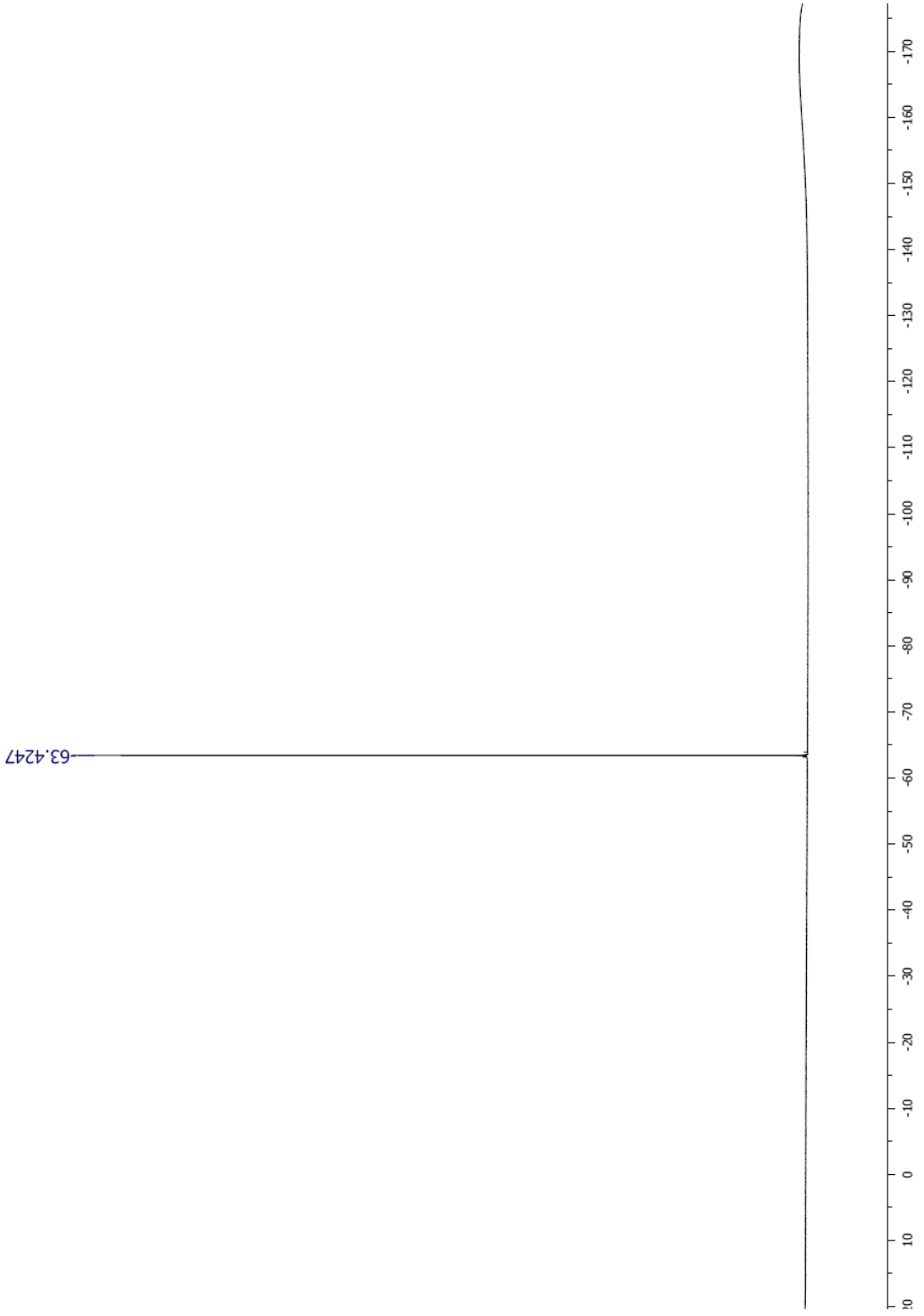

21.183
26.559
27.970
28.675
31.918
32.859
37.442
110.481
120.431
122.117
128.208
128.606
129.548
131.349
133.369
133.417
134.001
136.425
145.554
149.715
155.977
197.534
77.160

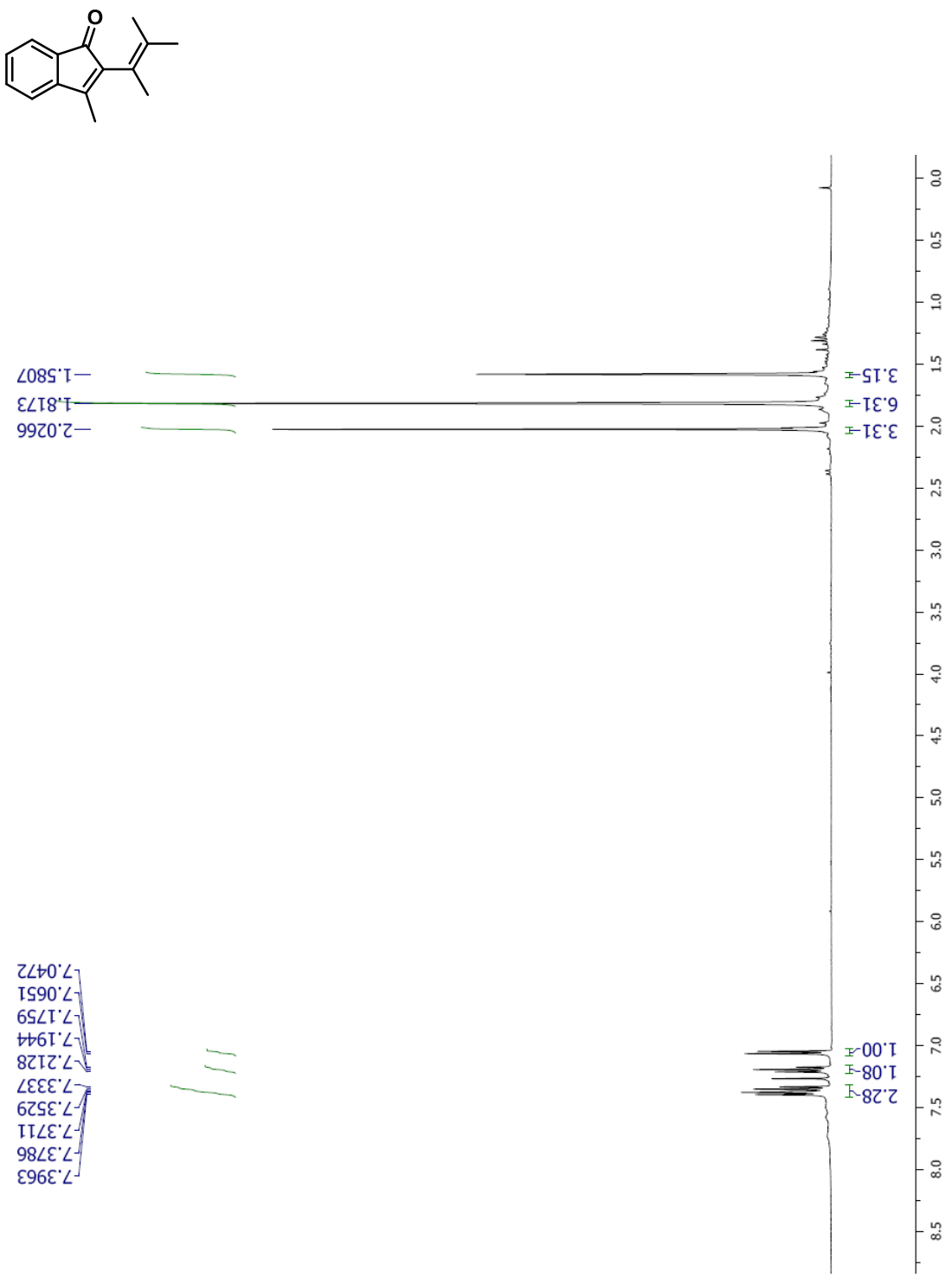

O
F3C

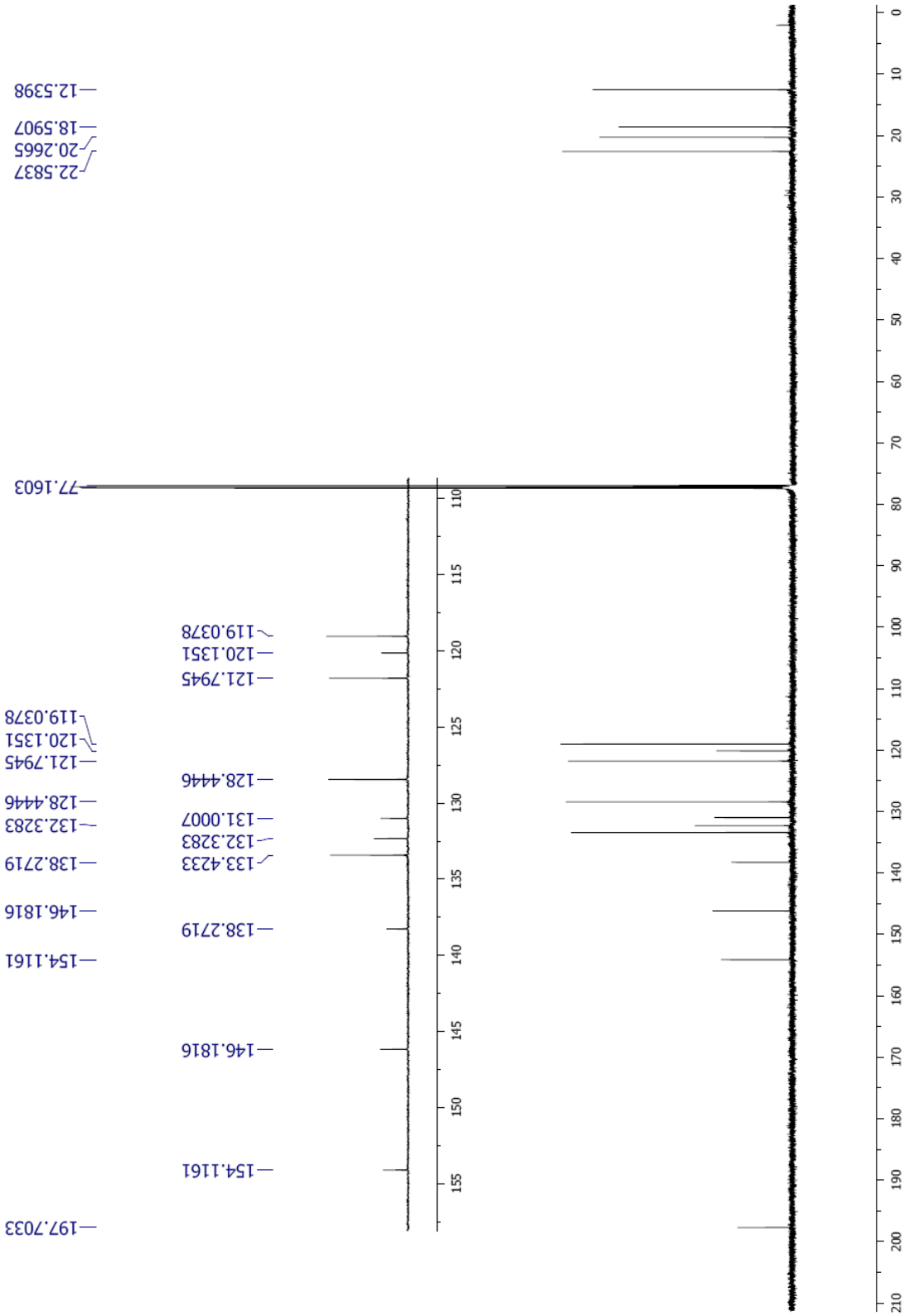

1.5355
1.5655
1.5925
1.6058
1.6242
1.6375
1.6516
2.1179
2.1311
2.1460
2.2648
2.2790
2.2927
3.9419
5.7172
6.7805
6.7984
7.1357
7.1378
7.1552
7.1724
7.1747
7.2066
7.2098
7.2259
7.2276
7.2439
7.2469
7.3691
6.32
2.12
2.07
2.04
1.00
1.01
1.09
1.03
2.05
1.01
2.09


26.488
27.999
28.658
31.966
32.970
37.447
110.186
120.147
122.463
77.160
124.286
125.829
128.522
129.019
129.375
131.131
133.568
134.073
110.186
120.147
122.463
124.286
125.829
128.522
129.019
141.421
150.356
154.290
197.114
141.421
145.132
150.356
154.290

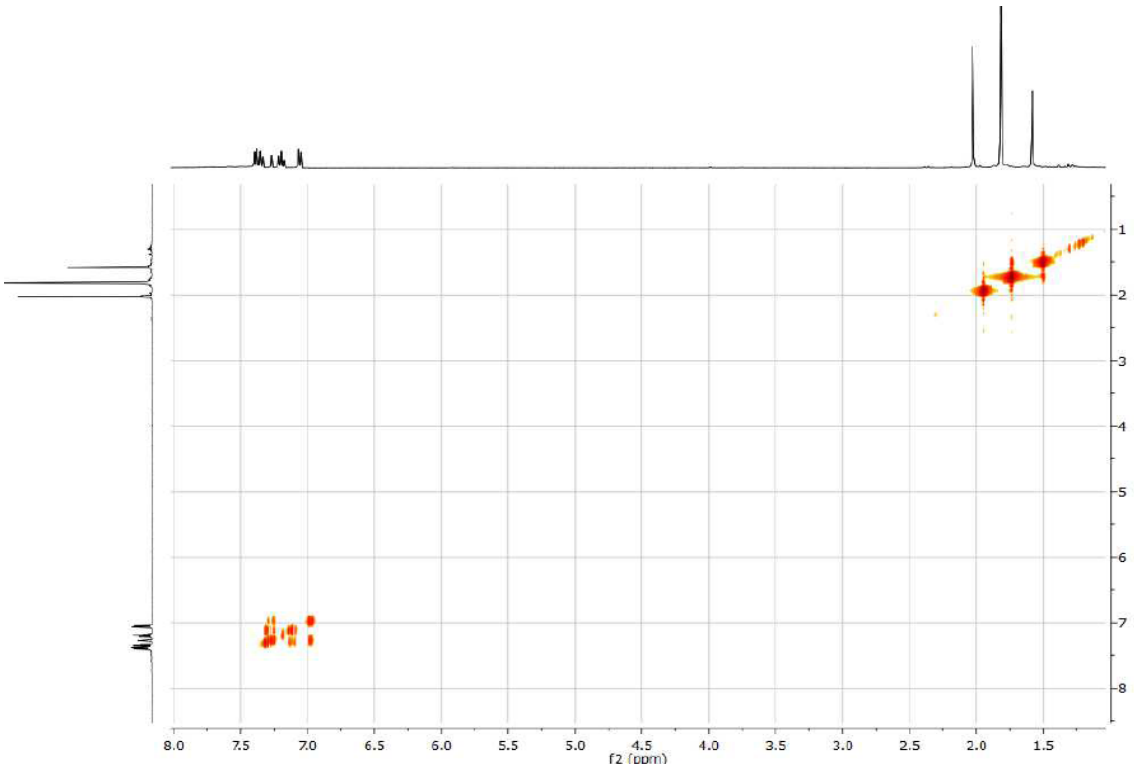
^{19}FNMR (376 MHz)



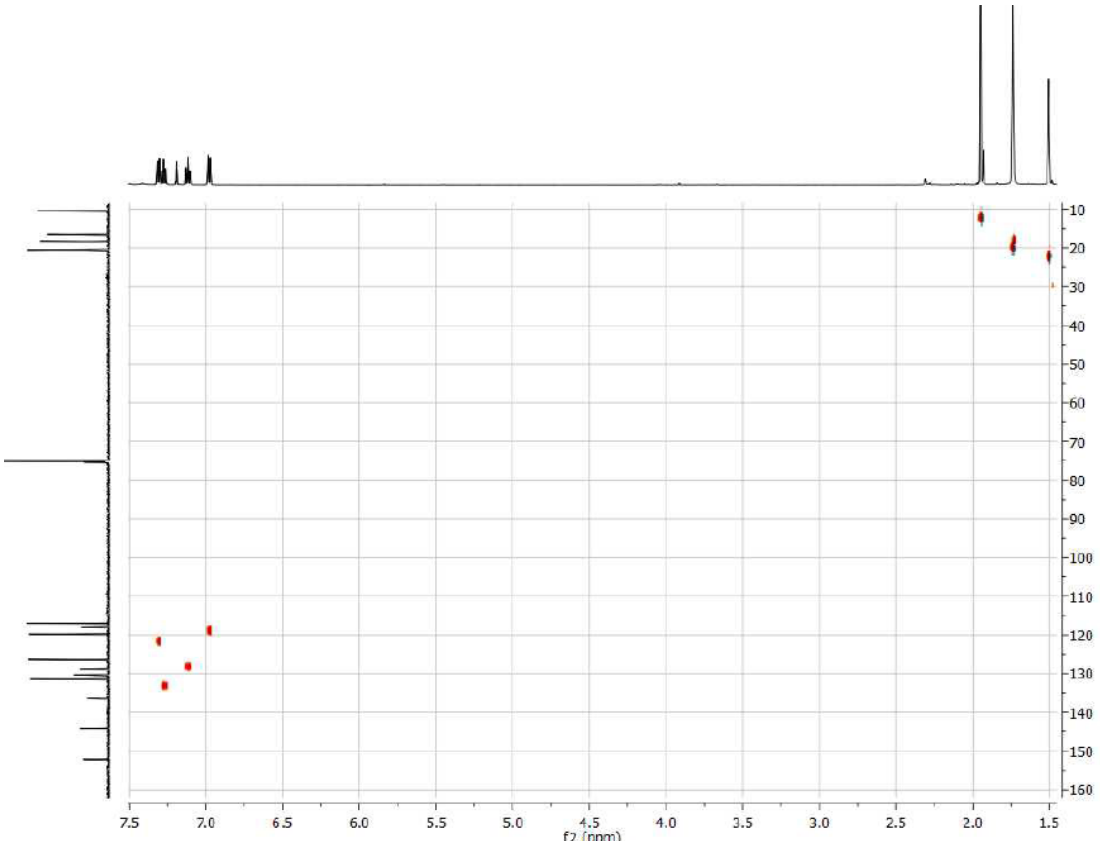

O
1.5807
1.8173
2.0266
3.15
6.31
3.31
7.0472
7.0651
7.1759
7.1944
7.2128
7.3337
7.3529
7.3711
7.3786
7.3963
1.00
1.08
2.28


12.5398
18.5907
20.2665
22.5837
77.1603
119.0378
120.1351
121.7945
128.4446
131.0007
132.3283
133.4233
138.2719
146.1816
154.1161
197.7033

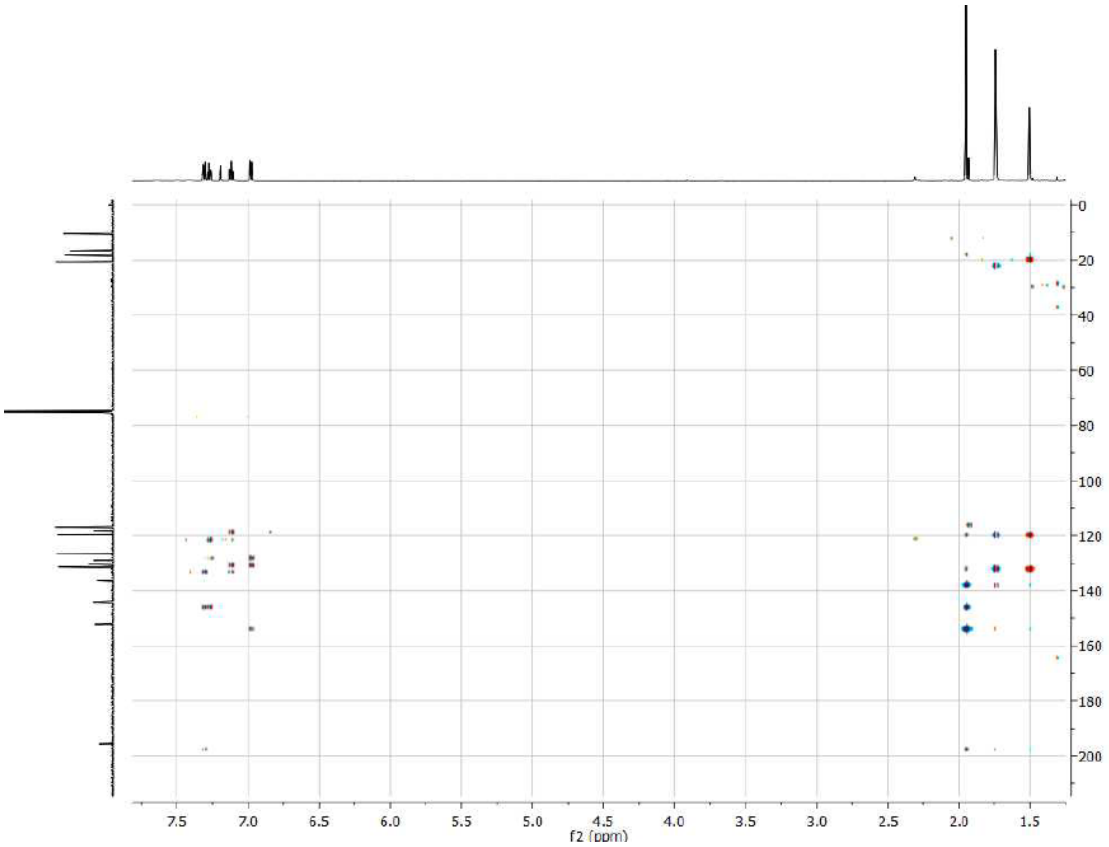
^{1}H COSY (400 MHz)

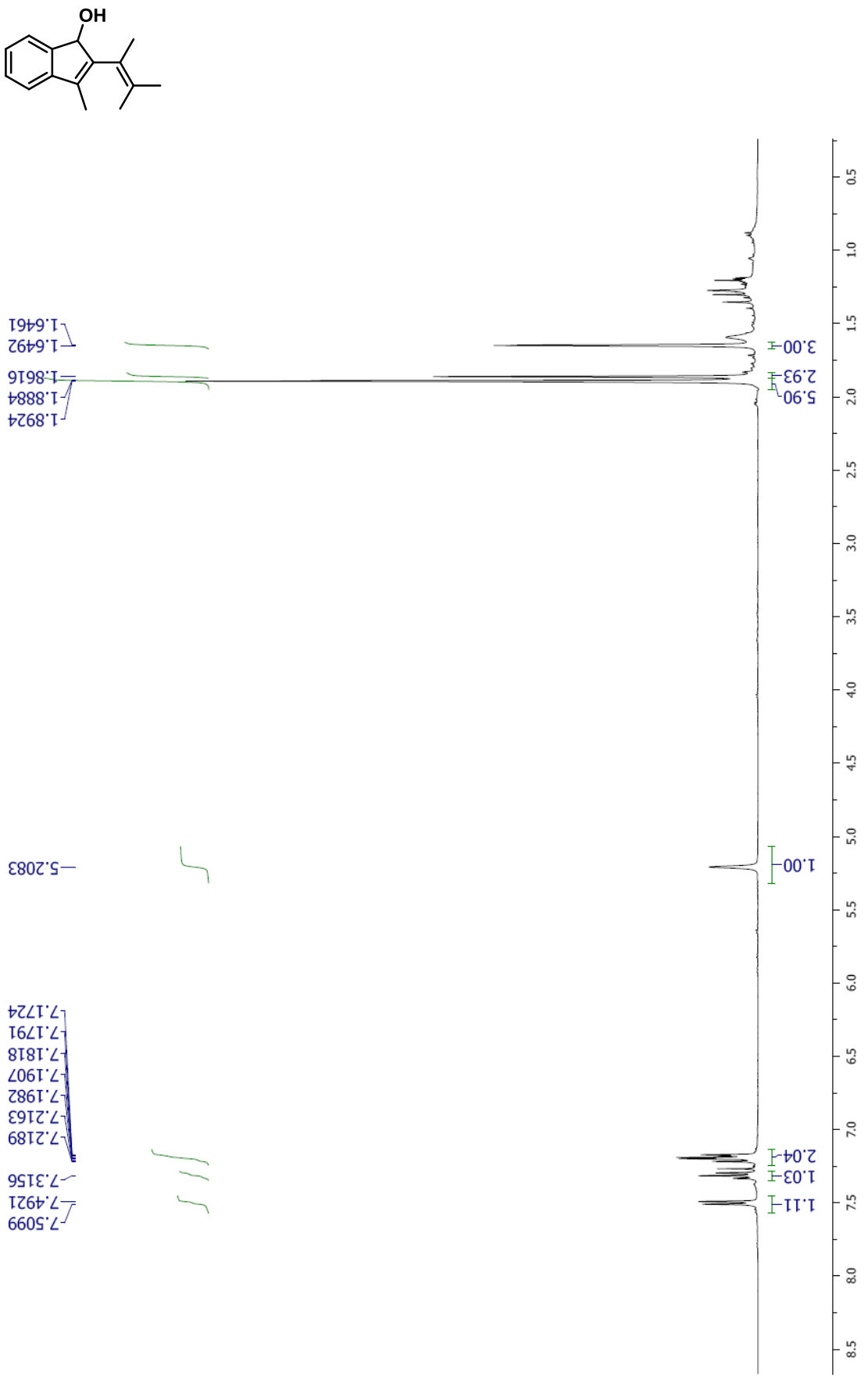


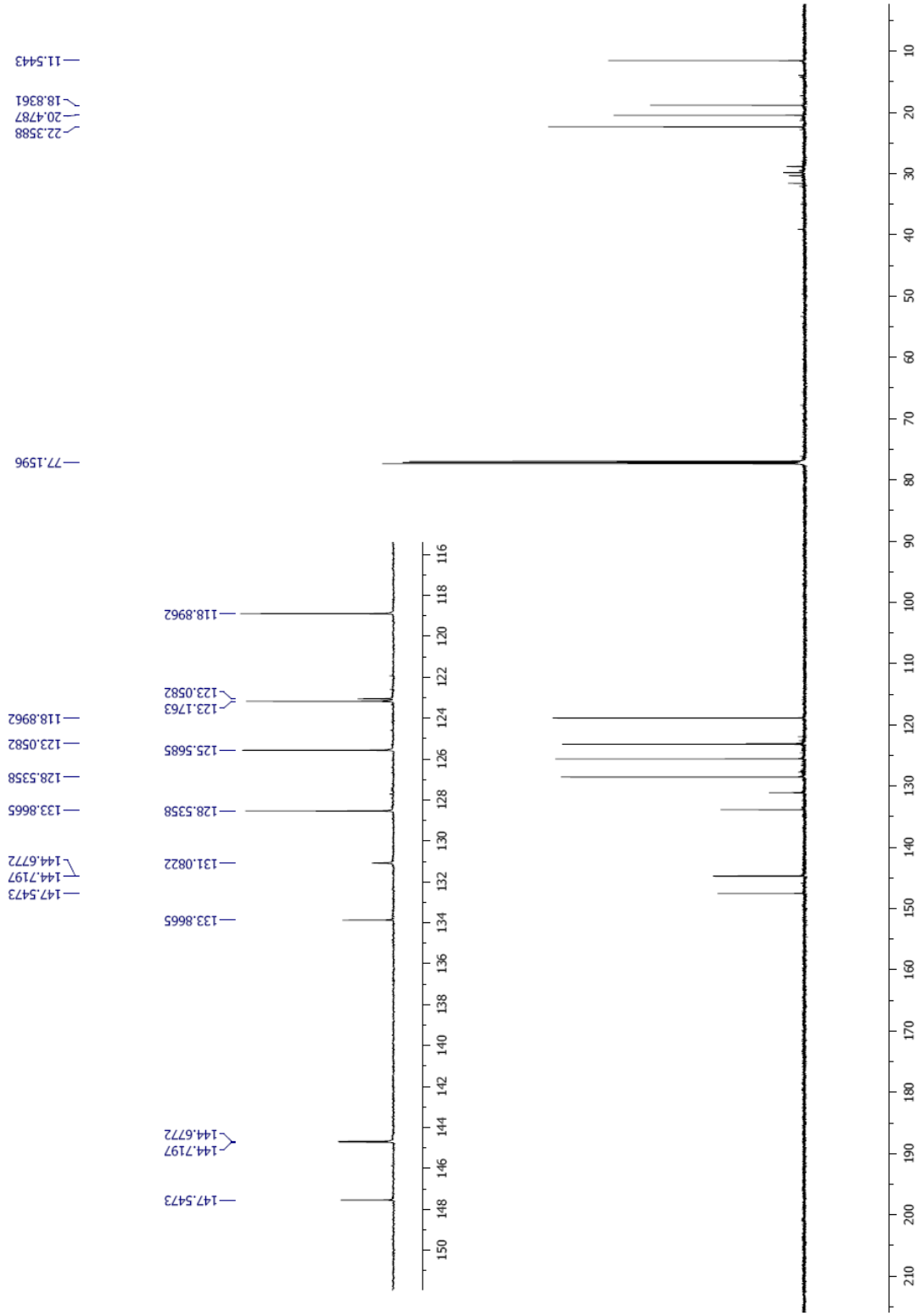
^{1}H-^{13}C HSQC (600 MHz)



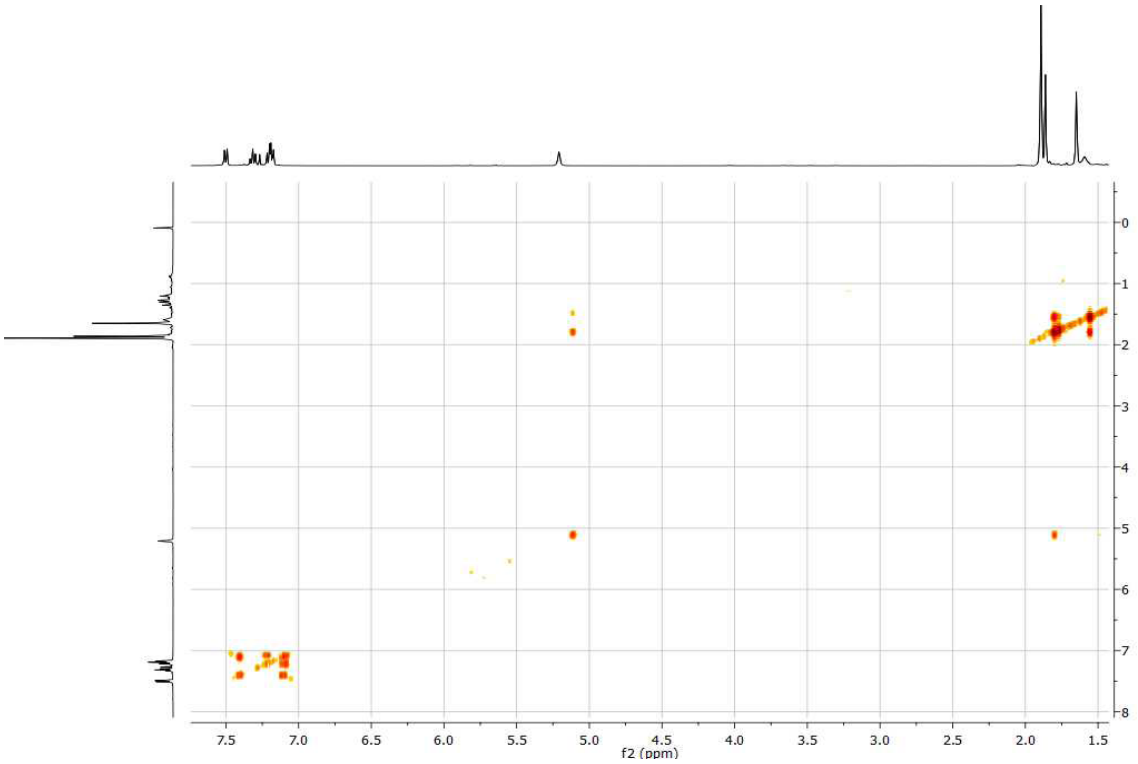
^{1}H-^{13}C HMBC (600 MHz)



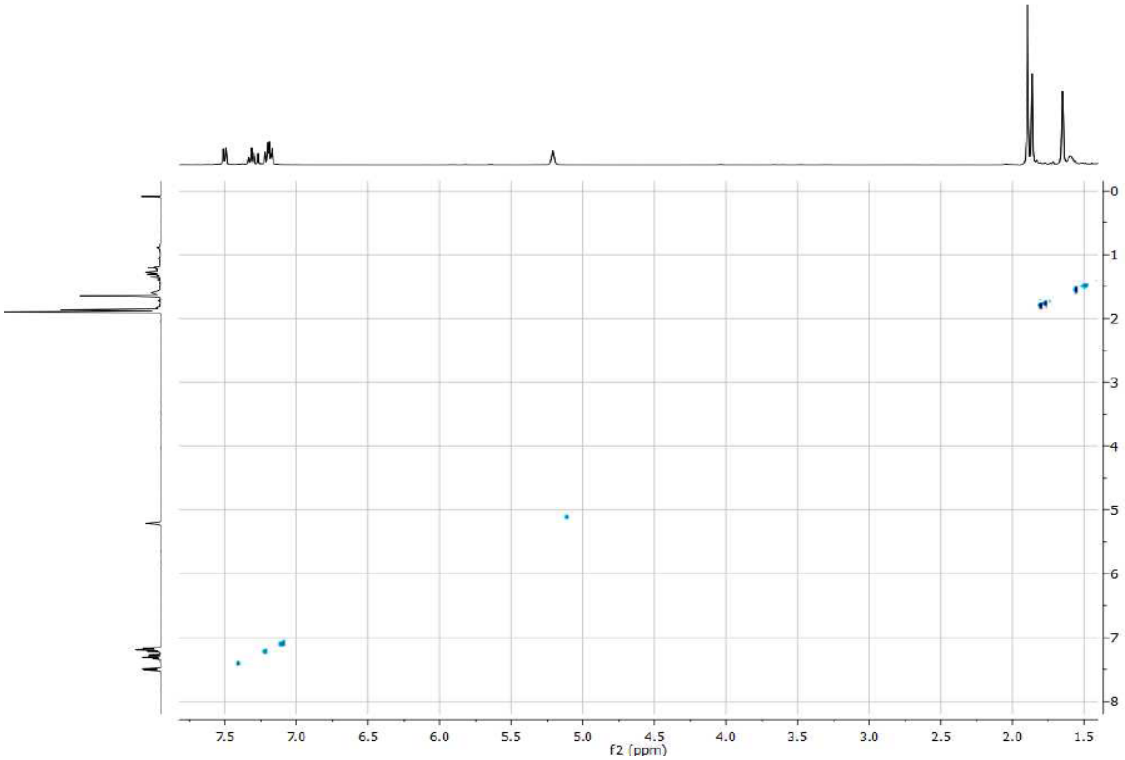



11.5443
18.8361
20.4787
22.3588
77.1596
118.8962
123.0582
123.1763
125.5685
128.5358
131.0822
133.8665
144.6772
144.7197
147.5473

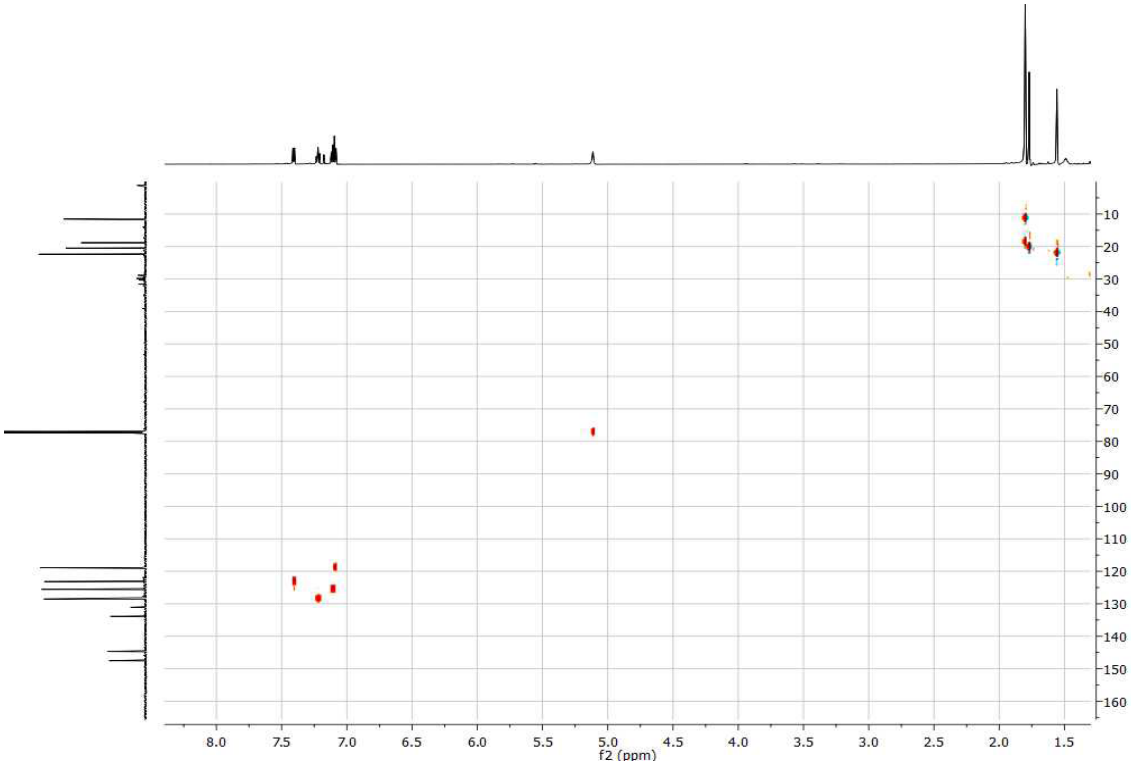
^{1}H COSY (600 MHz)



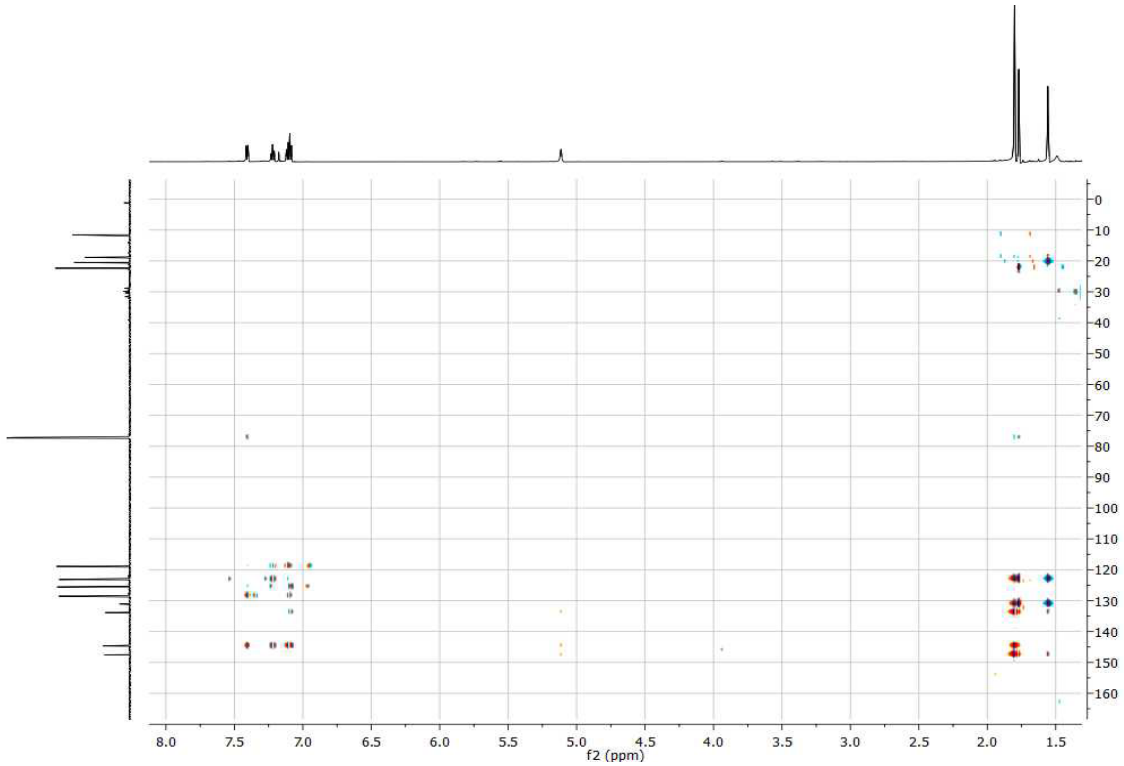
^{1}H NOESY (600 MHz)



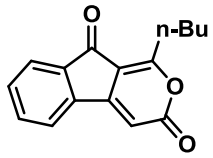
^{1}H-^{13}C HSQC (600 MHz)



^{1}H-^{13}C HMBC (600 MHz)



4. X-ray molecular structures



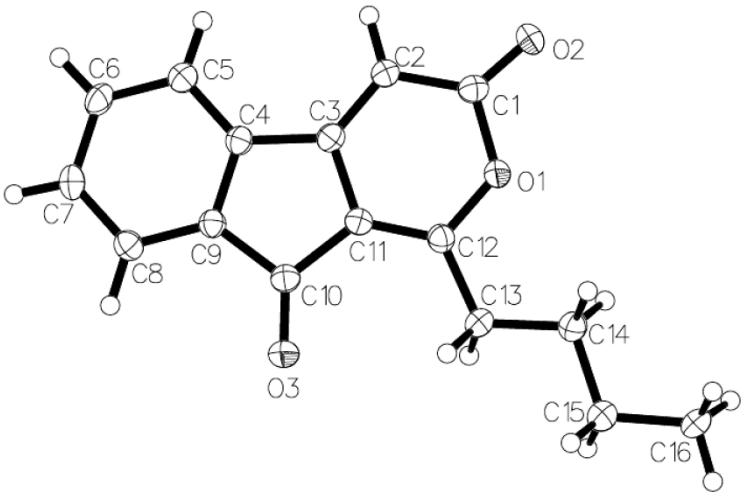
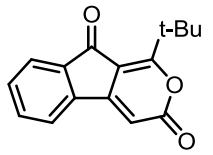


Figure S1 Molecular structure of 1-butylindeno[2,1-c]pyran-3,9-dione (2a) CCDC-852796



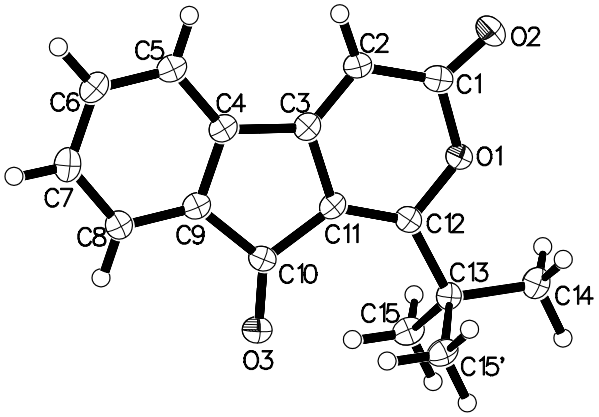


Figure S2 Molecular structure of 1-tert-butylindeno[2,1-c]pyran-3,9-dione (2c) CCDC-857641

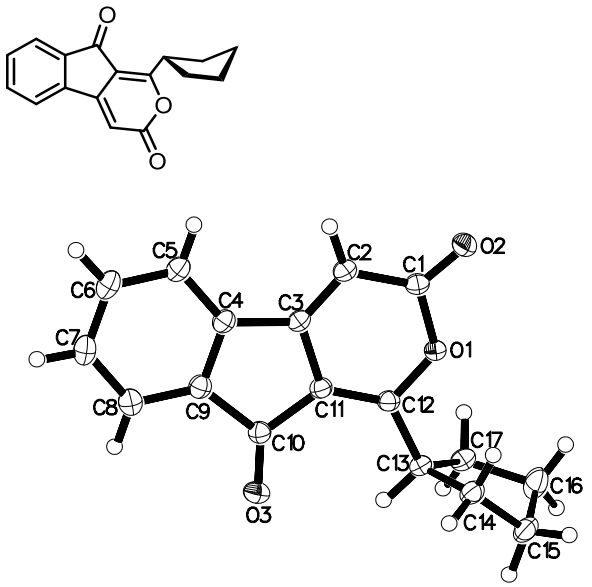


Figure S3 Molecular structure of 1-cyclopentylindeno[2,1-c]pyran-3,9-dione (2d) CCDC-857642

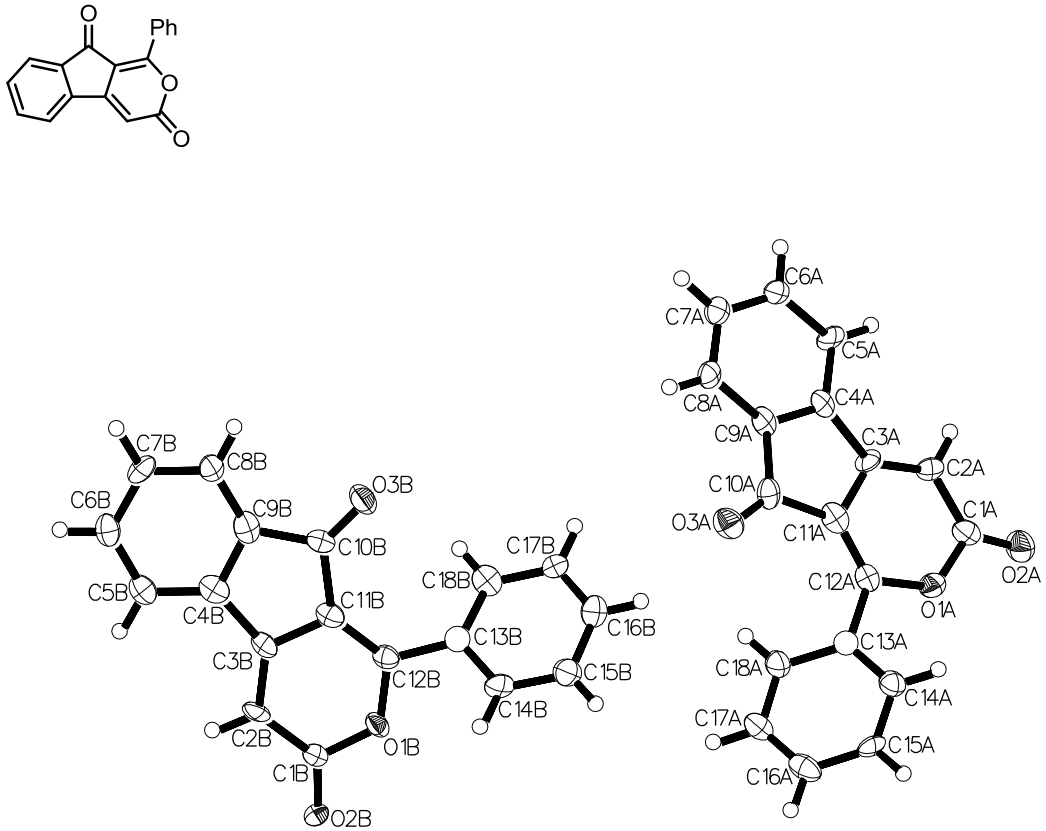


Figure S4 Molecular structure of 1-phenylindeno[2,1-c]pyran-3,9-dione (2k) CCDC-895772

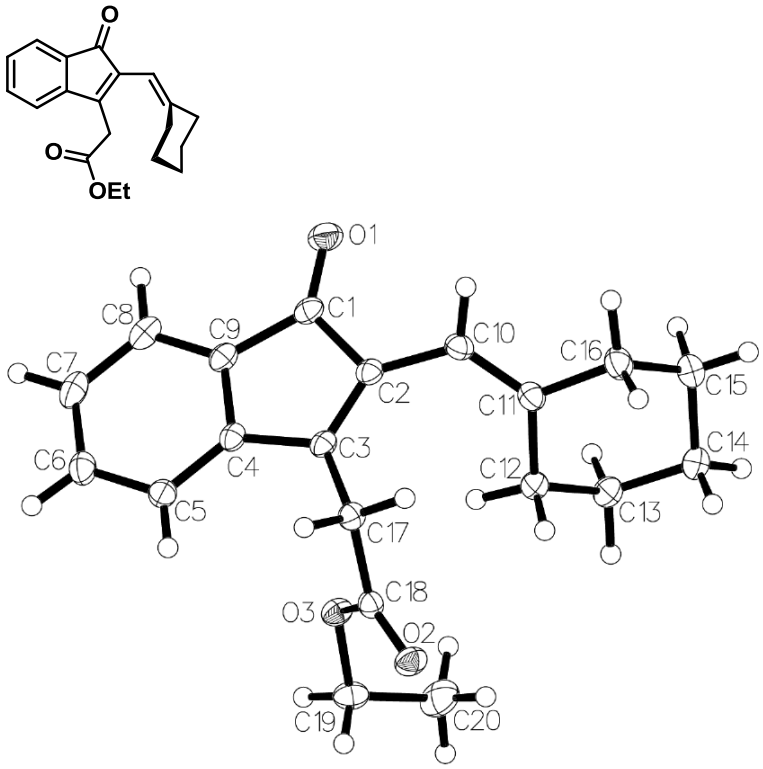


Figure S5 Molecular structure of ethyl 2-(2-(cyclohexylidenemethyl)-1-oxo-1H-inden -3-yl)acetate (3e)
CCDC-852797